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Thermodynamic Experiments and Modelling of Cyclopentane Hydrates in the Presence of NaBr, KBr, K₂SO₄, NaBr–KBr, NaCl–NaBr, KCl–KBr, Na₂SO₄–K₂SO₄, and CaCl₂–MgCl₂

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Abstract

Water shortage has been a serious issue for many years. Hydrate-based desalination (HBD) technology is a potential candidate for this solution. The present study investigates the use of Cyclopentane (CP) as a hydrate former for desalination through crystallization at low temperatures and atmospheric pressure. The primary objective of this work is to provide phase equilibrium data for CP hydrates (CPH) in the presence of novel salt systems, including NaBr, KBr, K₂SO₄, NaBr–KBr, NaCl–NaBr, KCl–KBr, Na₂SO₄–K₂SO₄, and CaCl₂–MgCl₂. Phase equilibrium temperatures were determined using both rapid and slow dissociation procedures. The van der Waals and Platteeuw-based Kihara (Kihara) approach, Hu-Lee-Sum (HLS) correlation, Standard Freezing Point Depression (SFPD) approach, and Activity-Based Occupancy Correlation (ABOC) were applied to model these new experimental data. The experimental results demonstrate that the differences between the quick and slow procedure data range from 0 °C to 1.2 °C. In addition, the increasing salt concentration enhances the inhibitory effect on hydrate formation. Furthermore, the influence of cations on the equilibrium temperature follows the decreasing order of Mg²⁺ > Ca²⁺ > Na⁺ > K⁺. In terms of halide anions, Br[−] exhibits a stronger impact on equilibrium temperature compared to Cl[−]. The thermodynamic modeling results (for all four models) show good agreement with the experimental data with the average absolute deviation (AAD) of less than or equal to 0.79 °C. The ABOC approach proves to be the most effective among the four methods evaluated for accurately reproducing the equilibrium temperature of CPH, with AAD less than or equal to 0.38 °C.

Keywords: HBD; CPH; phase equilibrium; salt inhibition effect; thermodynamics; modelling



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1. Introduction

In the context of global warming and climate change, both quantity and quality of natural resources are dwindling. Water security and the issue of water shortage have emerged

as one of the biggest global threats. Consequently, there is an urgent need for research and innovation aimed at optimizing water treatment and desalination processes. Among the emerging technologies under investigation, the HBD process has gained attention as a promising and potentially efficient solution.

Clathrate hydrates, also known as hydrates, are nonstoichiometric ice-like crystalline compounds composed of guest molecules that are trapped by hydrogen-bonded cages built up from the water molecules [1]. Water molecules are also called host molecules. Meanwhile, guest molecules are referred to as “former” or “promoter” molecules. There are many different guest molecules, ranging from small nonpolar gaseous molecules such as CO₂, H₂, CH₄, and N₂ to heavier polar molecules with large hydrophobic moieties including CP, tetrahydrofuran (THF), neohexane, etc. The kind of hydrate structure depends on the size and nature of the guest molecules. There are three main polymorphs of hydrates: cubic structure I (sI), cubic structure II (sII), and hexagonal structure H (sH) [1–3]. The unit cell of sI—the most common cubic structure—is constructed from 46 water molecules forming two small and six large cavities where the guest molecules can occupy. sII comprises 136 water molecules, making sixteen small and eight large cavities. However, the hydrate structure of type H is significantly more complex and much less common.

Hydrate formation is not a chemical reaction but only a physical phase change, which occurs most favorably at high pressure and low temperature. No chemical bonds or strong forces exist between the guest and host molecules. Therefore, guest molecules are free to rotate inside the cages built up from host molecules through van der Waals-type dispersion forces. All previous investigations indicate that hydrate formation is believed to occur in two steps: nucleation at the interface and growth, which depend on the temperature, the presence of surfactant, or the properties of the wall surfaces [1–4]. While the formation process has an exothermic nature, hydrate dissociation is an endothermic process. Heat must be supplied externally to break the hydrogen bonds between water molecules and the van der Waals interaction forces between the guest and water molecules of the hydrate lattice to decompose the hydrate to water and gas (or liquid).

In the past two decades, the potential of clathrate hydrate for solving problems in many industrial fields has been revealed and received notable interests. Indeed, hydrates have been extensively studied and investigated, and hydrate-based application technologies play an essential role in many applications in both science and engineering aspects. Owing to the ability to trap guest molecules and also the selective property, hydrate presents a vast potential for gas separation, storage, and transportation [2,5–8]. Hydrate-based technologies are also well-known as eco-friendly methods in CO₂ capture and storage [9–12]. Moreover, hydrates can be good candidates in cold storage and transportation as a replacement method for conventional refrigerants [13–15]. Furthermore, thanks to the hydrate formation and dissociation process, HBD is a promising, sustainable, novel method that has attracted special interest [16–25].

The concept of using hydrates for seawater desalination has been present for many decades. This technique was proposed for the first time in the 1940s by Parker who used R-23 as the hydrate former [26]. This proposal demonstrated, in theory, the feasibility of desalination through hydrate formation. As mentioned previously, the principle of HBD is based on a liquid-to-solid phase change. During this process, only pure water is involved in the crystallization of hydrate, and salt ions and other impurities are excluded from the solid phase (hydrate) and remain in the concentrated aqueous solution. In other words, salts are not incorporated into the hydrate structure. Then, following the formation of hydrates, the hydrate crystals can be separated from the residual brine solution using filtration or other separation techniques. Desalinated water and guest molecules can be recovered upon the dissociation of the separated hydrate crystals [27–29].

Given the ability of hydrates to be formed at higher temperatures than the freezing point of ice, the process is expected to require less energy and improve energy efficiency. Ho-Van et al. [17] analyzed critical aspects such as energy consumption, the efficiency of water production, and the economy of desalination plants between HBD and traditional technologies. They pointed out that the production cost associated with HBD is considerably lower than multi-stage flash distillation, solar thermal distillation, freezing, and ion-exchange desalination technologies. Despite these advances, safety operation conditions and guest molecule separation methods remain challenges for applying this technique in desalination plants. These challenges can be overcome by selecting a suitable guest molecule on which the operating conditions are highly dependent.

The most commonly studied guest molecules in desalination applications include methane (CH_4), carbon dioxide (CO_2), propane (C_3H_8), hydrofluorocarbons (HCFC), chlorofluorocarbon refrigerants (e.g., R141b), CP, and THF [17,24]. Among these, light hydrocarbons, CO_2 , HCFC, and R141b have been shown to enhance salt removal efficiency. However, these guest molecules require high pressure to operate, which poses a significant challenge in practical implementation. In contrast, CP and THF are two guest molecules that can form hydrates at atmospheric pressure and an accessible temperature. Due to its high solubility, THF is miscible in water, complicating the separation and recovery process after hydrate dissociation. CP shows a better-promoting effect than THF [25]. Furthermore, with the immiscible properties in water, it is also easy to separate CP from dissociated water to recover and recycle.

CP is a well-known guest molecule capable of forming hydrates with pure water at ambient pressure and temperatures ranging approximately from 6.3 °C to 7.8 °C, depending on the experimental method used. Ho-van et al. revealed that the equilibrium temperature range of 6.6 °C to 7.2 °C seems the most reliable [17]. Due to its size, CP forms sII hydrate and only occupies the large cages ($5^{12}6^4$ cages), leaving the small cages empty. Therefore, the theoretical composition (guest/water ratio) of CPH is 1:17. With the help of gases, CP still forms sII hydrate under pressure. Several researchers obtained equilibrium datasets of CPH in the presence of NaCl [30–36]. Numerous phase equilibrium data of CPH in the presence of single salts (KCl, CaCl_2 , MgCl_2 , and Na_2SO_4) and mixture solutions (NaCl-KCl, MgCl_2 -NaCl, MgCl_2 -NaCl-KCl) were reported [27,30].

A comprehensive understanding of phase equilibrium data of CPH in the presence of electrolytes is crucial for the practical implementation of CPH-based desalination in commercial use. More thermodynamic data of CPH in the presence of new salt systems at different concentrations can help provide a better understanding of HBD processes in real-world conditions. From a practical perspective, phase equilibrium analysis supports the design and scaling of CPH-based desalination systems for general saltwater, ensuring reliable operation and consistent water quality. It provides quantitative guidance for process optimization, prevents premature material saturation, and enhances overall system performance. Consequently, integrating detailed thermodynamic and equilibrium data into the design of CPH-based desalination units is pivotal for bridging the gap between laboratory research and commercial application, offering a viable approach to large-scale, energy-efficient saltwater treatment.

The previous studies did not address the thermodynamics of CPH in the presence of diverse salts and their mixtures in the wide range of concentrations. This research will provide additional experimental data and validate the thermodynamic models for new salt systems (single and multi-salt solutions). Such advancements are crucial for kinetic studies, which play a key role in designing industrial desalination systems. Given the limited available data, the primary objective of this study is to expand the experimental phase equilibrium data of CPH in the presence of various electrolytes—namely NaBr, KBr,

K_2SO_4 , NaBr – KBr , NaCl – NaBr , KCl – KBr , Na_2SO_4 – K_2SO_4 , and CaCl_2 – MgCl_2 —which are common salts in seawater or major contributors to water hardness. These measurements are conducted at multiple concentrations using both quick and slow dissociation procedures. Then, four thermodynamic modeling approaches are performed to accurately predict the CPH equilibrium points in a brine solution: Kihara approach, HLS correlation, SFPD method, and ABOC.

2. Materials and Methods

2.1. Materials

Table 1 lists all the materials used in this work. CP is supplied by Aladdin Biochemical Technology Co., Ltd., (Shanghai, China) while the NaBr , K_2SO_4 , $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, and $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ are provided by Sigma-Aldrich, Co., (St. Louis, MO, USA) and the KBr , Na_2SO_4 , KCl , and NaCl are provided by Fisher Scientific, (Loughborough, UK). Ultrapure water with a resistivity $\rho \approx 0.055 \text{ m}\Omega \cdot \text{cm}$ and TOC (total organic carbon content) less than 4 ppb is supplied by the Milli-Q[®] Advantage A10 Water Purification System (Merck, Darmstadt, Germany).

Table 1. Purity of initial material used.

Material	Chemical Formula	Mol. Weight (g/mole)	Solubility in Water (g/L)	Purity
CP	C_5H_{10}	70.13	0.156 (25 °C) [37]	96%
Sodium bromide	NaBr	102.89	900 (20 °C) [38]	98%
Potassium bromide	KBr	119.00	678 (25 °C) [38]	99.5%
Sodium sulfate	Na_2SO_4	142.04	280 (20 °C) [38]	99.5%
Potassium sulfate	K_2SO_4	174.26	110 (20 °C) [38]	99%
Calcium chloride	$\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$	110.98	420 (20 °C) [38]	99%
Magnesium chloride	$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$	95.21	546 (20 °C) [38]	98%
Potassium chloride	KCl	74.55	340 (20 °C) [38]	99%
Sodium chloride	NaCl	58.4	360 (20 °C) [38]	99.5%

2.2. Apparatus

A series of experiments of quick and slow dissociation procedures, are conducted in two distinct apparatuses, as illustrated in Figures 1 and 2, respectively.

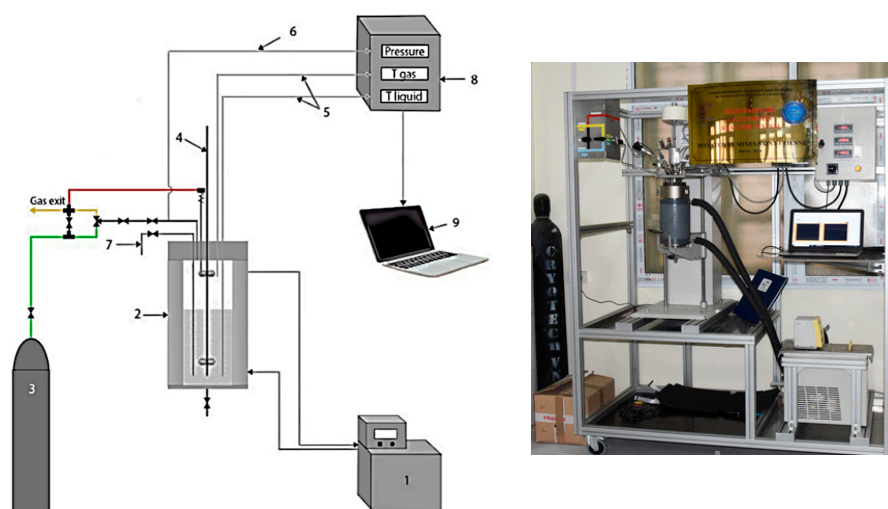


Figure 1. Simplified schematic diagram of the main experimental apparatus for the quick dissociation procedure (noted that in this work, we do not use a gas bottle and valve system). 1—Chiller, 2—Vessel, 3—Gas bottle, 4—Agitator, 5—Temperature probe, 6—Pressure probe, 7—Liquid sampling, 8—Transmitter, 9—Computer.

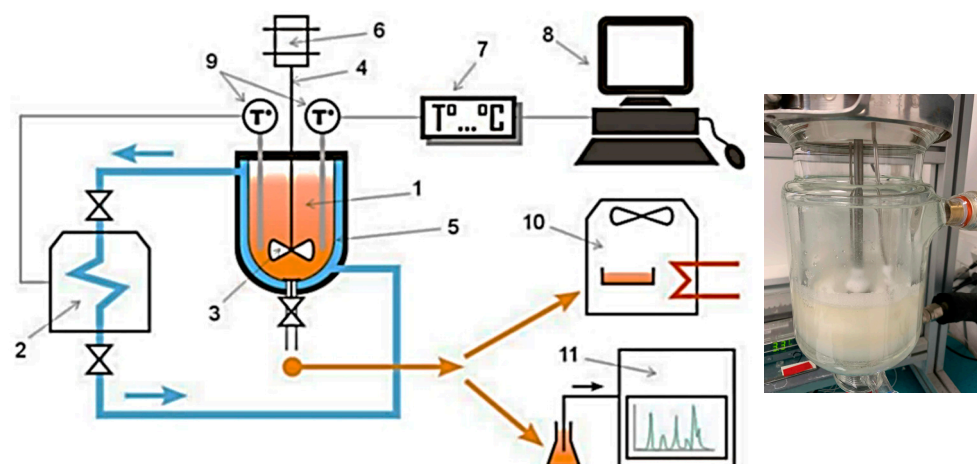


Figure 2. Simplified schematic diagram of the main experimental apparatus for the slow dissociation procedure. 1—Vessel, 2—Chiller, 3—Impeller, 4—Agitator, 5—Cooling jacket, 6—Motor, 7—Temperature transmitter, 8—Computer, 9—Temperature probe, 10—Drying oven, 11—Ion chromatography. Reprinted with permission from Ho-van et al. [30].

In the case of experiments involving quick dissociation procedures, the reactor is a cylindrical vessel provided by PARR Instrument Company with an inner volume of 1.35 L. The chiller RE307 constantly and uniformly controls the temperature inside the vessel via a double jacket. This chiller is furnished by Lauda Ecoline with a temperature accuracy of ± 0.1 °C. The coolant of the chiller is a solution of water and ethanol (50% by mass fraction).

In contrast, the experimental setup for the slow dissociation procedure is the same as described by Ho-Van [30]. The reactor is a jacketed batch glass vessel supplied by Verre Equipment with an approximate inner volume of 1 L. A double jacket has been installed around the vessel to ensure constant and uniform temperature control. The Ministat 240, supplied by Huber (Edison, NJ, USA), is the chiller utilized in this procedure, and it boasts a temperature stability of ± 0.02 °C.

In both systems, the agitator inside the vessel is driven by a motor, thereby mixing the injected solution. Probes monitor the solution's temperature, which is subsequently transmitted to the computer by a transmitter. LabVIEW records the data obtained throughout the experiment.

The salt concentration of the samples taken in the experiment is measured using a drying oven and ion chromatography device.

2.3. Quick Dissociation Procedure

The quick dissociation process developed by Ho-Van et al. [30] aims to rapidly estimate the temperature equilibrium. The initial step of this procedure is to disassemble the reactor, followed by a thorough cleaning of the reactor and all beakers with deionized water to ensure the removal of any residual contaminants. Then, a solution containing 400 mL of deionized water and a quantity of salt (depending on the chosen concentration) is prepared and mixed well for 10 min. A 5 mL sample of salt solution is taken to measure the concentration. The prepared solution is injected into the reactor, followed by 121.54 mL of CP. This proportion is based on the theoretical stoichiometric composition of CPH $n_{\text{water}}/n_{\text{CP}} = 17$ [1]. Subsequently, the solution is stirred continuously at a 400–500 rpm rate thanks to the agitator. The Cryostat or cooling system operates at a set point above the freezing point of the salt solution to guarantee no ice formation in the solution. As the temperature of the solution approaches the set point, a small quantity of ice, prepared previously from deionized water, and an appropriate quantity of salt are introduced into the reactor. The addition of ice acts as a nucleating agent to initiate the crystallization

process, while introducing salt maintains the salt concentration constant. Because it is not possible to see directly inside the reactor, after the formation of CPH (based on the temperature profile) the temperature is kept stable for approximately 3–4 h to ensure a sufficient amount of CPH is formed. The cryostat is then switched off. Due to the heat from the surrounding environment, CPH dissociates progressively. Then, the temperature surges dramatically. The bending point is considered as the equilibrium temperature of the prepared salt concentration. Also, the agitator is stopped at that time to separate the salt solution phase from the CP phase. A 5 mL brine solution sample is collected through liquid sampling to cross-check with the previous sample. When the two salt concentrations were identical, with an error below 3%, the equilibrium temperature was reported. The quick dissociation methodology can be described briefly by steps as follows (Figure 3):

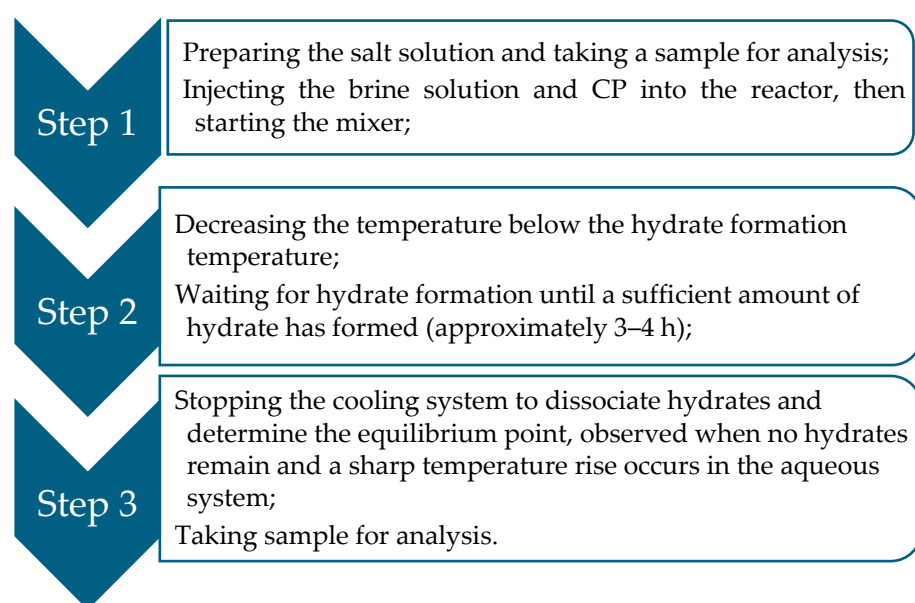


Figure 3. Quick CPH dissociation procedure for determining thermodynamic equilibrium.

2.4. Slow Dissociation Procedure

The slow dissociation procedure experiment is performed with the same salt concentration as each quick dissociation experiment. The objective of this procedure is to provide more accurate data and cross-check with quick dissociation procedure data. The solution is mixed continuously at 300–400 rpm throughout the experiment. The experimental steps are carried out similarly to the quick procedure until sufficient CPH has been formed (which can be observed directly in the vessel). Then, the temperature is manually controlled via the cooling system. Initially, the temperature increases at an increment of 1 °C and remains constant for at least 1 h. When the temperature reaches a value of 3 °C lower than the equilibrium temperature obtained from the quick procedure, a series of 0.1 °C temperature increments are implemented and iterated until only a few hydrate particles are observed visually. The temperature is then maintained for an extended period, ranging from half a day to a day, to ensure that equilibrium is reached. This step is repeated as long as crystals are still present in the vessel. The equilibrium temperature is the one recorded in the penultimate step where CP, CPH, and aqueous phase coexist. At each step of increasing temperature, the image of the solution is recorded for analysis and comparison to find the temperature at which only two phases of salt solution and CP can be observed. To ensure that no CPH remains in the bulk at the final step of the procedure, a sample of 5 mL was taken from the bottom of the vessel. This sample is then used to compare the salt concentration at the initial stage (before cooling) and at the final stage (dissociation point).

Analyses were carried out using a drying oven set at 60 °C. If these two salt concentrations are identical (with an error of less than 1%), the equilibrium temperature is then recorded.

An uncertainty analysis was conducted by Ho-Van [30]. The uncertainty of temperature measurements is ± 0.1 °C. The uncertainty of mass balance measurements is 0.01 g, and the uncertainty for volume measurements is 0.01 mL. The uncertainty of salt concentration is: 0.002% mass due to weighing; 0.2% mass due to drying oven. All initial conditions in quick dissociation and slow dissociation experiments are listed in Appendix A (Tables A1 and A2). These tables present the pure salts and their mixtures tested in CPH experiments at concentrations ranging from 0% to 20% by mass corresponding to the amount of water, salt, and CP used. The slow dissociation methodology can be described briefly by steps as follows (Figure 4):

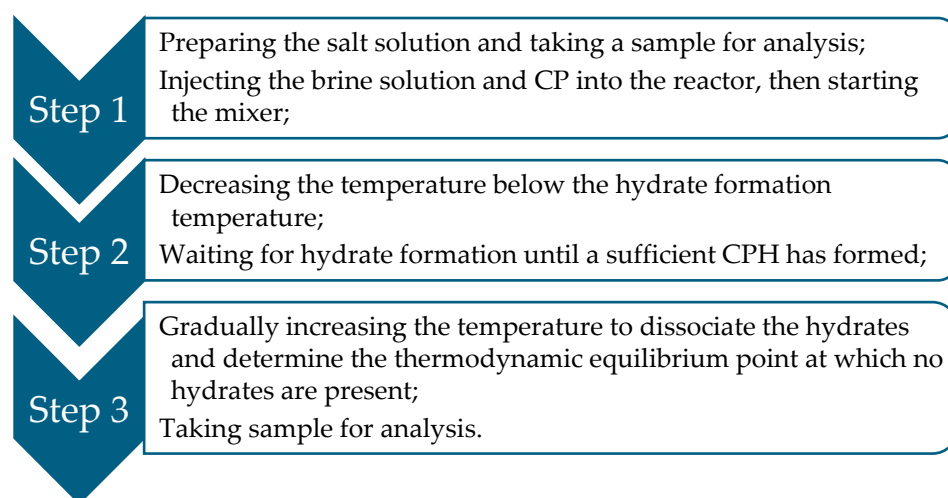


Figure 4. Slow CPH dissociation procedure for determining thermodynamic equilibrium.

3. Experimental Results

3.1. The Behavior of CPH Formation and Dissociation

Hydrate formation and dissociation processes are exothermic and endothermic, respectively [1]. These thermal characteristics make it possible to clearly identify and analyze both processes by monitoring temperature throughout the experiment. Figure 5 illustrates the standard temperature profiles of the quick dissociation experiment.

Upon the introduction of ice into the reactor (point 1), a slight increase in temperature was observed as a consequence of the exothermic nature of hydrate crystallization. When the chiller stopped (point 2), the temperature rose significantly as a result of heat transfer from the surrounding environment into the reactor. Subsequently, the slope of the temperature curve diminished, and the temperature remained relatively stable as the hydrate strongly dissociated (point 3). Theoretically, the temperature in this period should remain unchanged. However, the unstable temperature can be ascribed to either nonequilibrium dissociation or the existence of small hydrate blocks within the reactor. Thereafter, a dramatic surge in temperature occurred, indicating complete hydrate dissociation. The temperature at which the slope changed remarkably was recorded as the equilibrium temperature (point 4).

The quick dissociation experiment of CPH in pure water was repeated, and the equilibrium temperature was recorded at 7.3 ± 0.1 °C. This value is close (error less than 3%) to the published literature data, which records 7.1 °C [30]. Ho-Van et al. [30] declared that the quick dissociation procedure carries a risk of recording an equilibrium temperature that exceeds the actual equilibrium temperature itself. This discrepancy can be attributed to the higher heat transfer rate from the surrounding environment to the

liquid phase compared to the heat transfer rate from the liquid phase to the hydrate crystal. Additionally, as measured in our apparatus, the equilibrium temperature of CPH in pure water is slightly lower than the value of 7.7 ± 0.1 °C reported by Ho-Van [30] using the same quick dissociation procedure but in a different apparatus. It is noteworthy that our result approaches their value obtained through the slow dissociation procedure (7.0 ± 0.1 °C). Therefore, our quick experimental results offer a reliable first approximation and estimate.

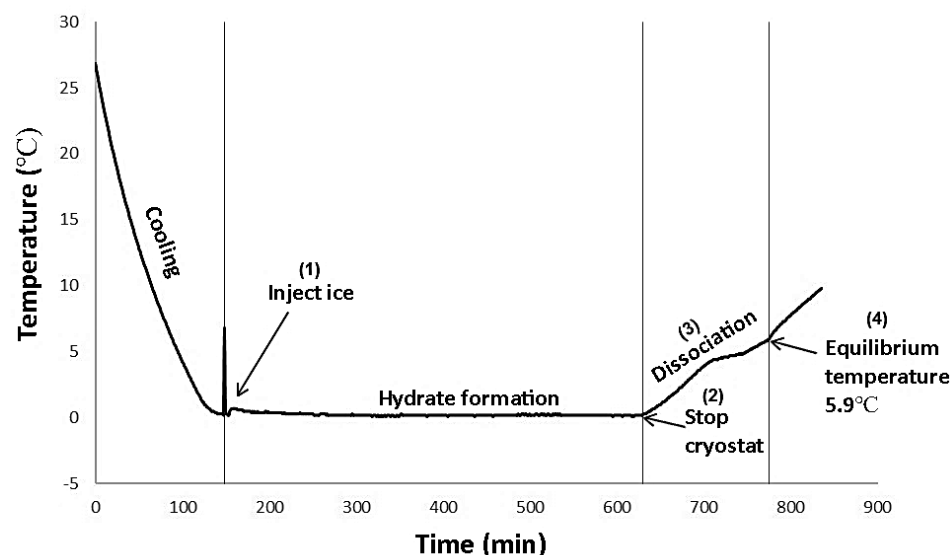


Figure 5. Standard temperature profiles of hydrate formation and dissociation in the quick dissociation procedure (in NaBr 5.0 wt.%).

Similarly to the quick experiment, the hydrate formation in the slow dissociation procedure started after the injection of ice, resulting in a slight temperature rise. However, the dissociation process is meticulously controlled and prolonged by gradually increasing the temperature and maintaining it for a minimum of one hour (Figure 6). It is expected that the equilibrium temperature can be determined with greater precision by decelerating the dissociation process, as presented by Ho-Van et al. [30].

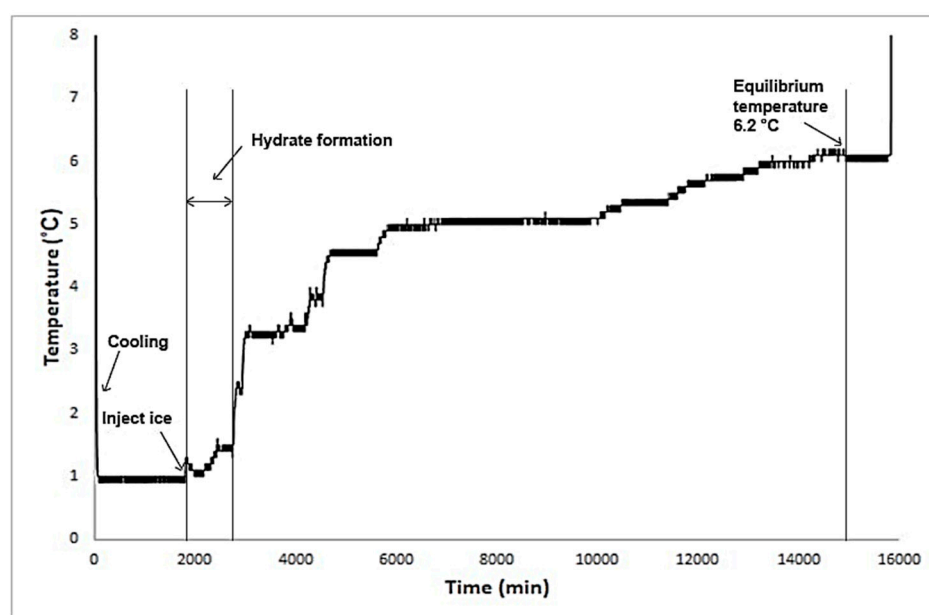


Figure 6. Standard temperature profiles of hydrate formation and dissociation in the slow dissociation procedure (in NaBr 3.5 wt.%).

3.2. Experimental Dissociation Data of CPH in the Presence of Salts

The experimental results of CPH in the presence of NaBr, KBr, K_2SO_4 , NaBr-KBr, NaCl-NaBr, KCl-KBr, Na_2SO_4 - K_2SO_4 , and $CaCl_2$ - $MgCl_2$, which are common electrolytic salts found in seawater or are considered to be the primary cause of hard water, are summarized in Figures 7 and 8 (for further details, see Table A3 in Appendix B).

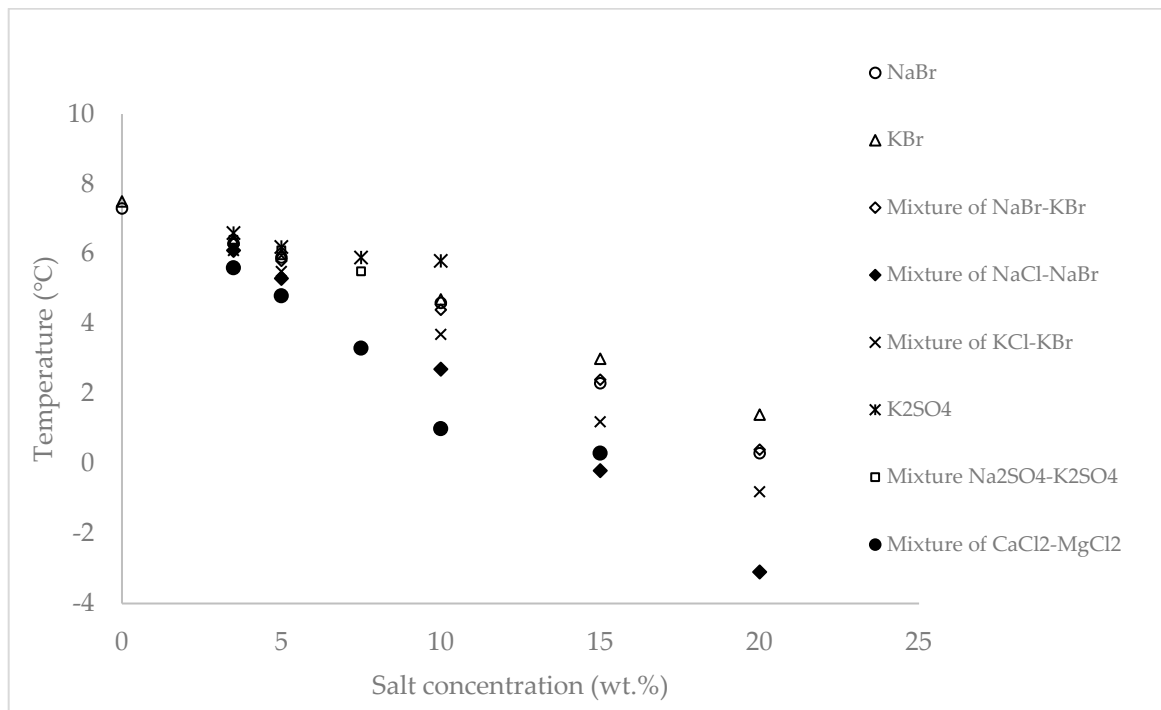


Figure 7. Equilibrium temperature of CPH in the presence of salts from the quick dissociation procedure.

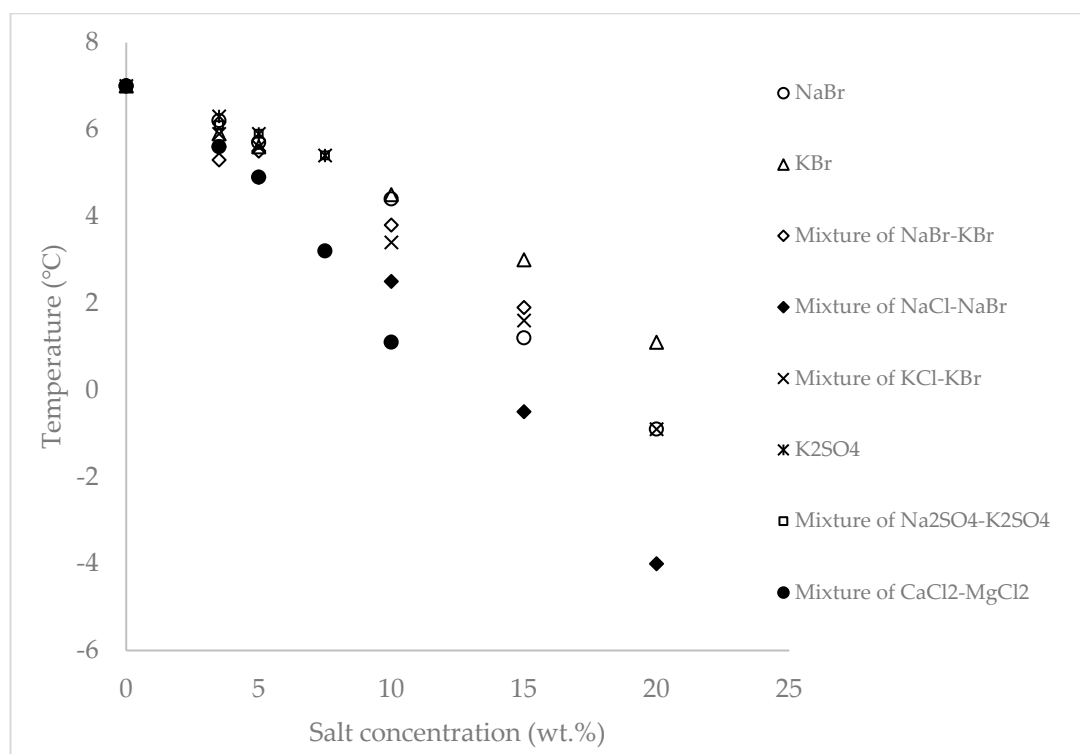


Figure 8. Equilibrium temperature of CPH in the presence of salts from the slow dissociation procedure.

As previously indicated by Ho-Van et al., in the slow procedure, a drying oven and/or ion chromatography were employed to verify the initial salt concentration and the salt concentration of the solution taken at the equilibrium temperature. If these two values are identical, no hydrate is present in the reactor, and the dissociation temperature is then recorded. Consequently, the results are considered accurate and valuable. For our investigation, the initial and final salt concentrations are nearly equivalent.

It can be clearly seen in Figures 7 and 8 that the experimental results following quick dissociation procedure are slightly higher than the values obtained by the slow dissociation procedure. The discrepancy between the measured data from both procedure ranges from 0 °C to 1.2 °C. Indeed, the quick dissociation procedure apparently misses and records moderately late the actual equilibrium. Therefore, equilibrium data is more reliable and consistent when obtained using a slower process than a quick one.

Several quick dissociation experiments in the presence of KBr and K₂SO₄ were repeated with different stirring speeds (400 rpm and 500 rpm). A slight difference was observed between the obtained equilibrium temperatures. A higher stirring speed (500 rpm) resulted in a decrease in equilibrium temperature of up to 0.9 °C compared to that observed at 400 rpm. It is hypothesized that higher stirring speeds may have resulted in more homogenous mixtures. This could have led to a kinetics change and a decrease in the difference between the heat transfer rate from the surrounding environment to the liquid phase and the heat transfer rate from the liquid phase to the hydrate crystal. For all quick dissociation experiments that were performed later, a stirring speed of 500 rpm was applied.

As illustrated in Figures 7 and 8, the equilibrium temperature is strongly influenced by the salt concentration for all tested salt systems. A clear downward trend is observed as the salt concentration increases. This behavior confirms that electrolytic salts significantly affect hydrate formation [1]. It is widely recognized that they function as natural hydrate inhibitors [1,2,4]. Electrolytes substantially impact water activity, thereby affecting the CPH phase equilibria. The interactions between salt ions and the polar water molecules lead to the formation of saltwater clusters, which inhibit water molecules from participating in the hydrate structure. Additionally, the salting-out phenomenon—where the solubility of a nonelectrolyte compound (CP, in this case) decreases as salt concentration increases—causes a shift in the equilibrium temperature. Consequently, as salt concentration rises, both the clustering effect and salting-out intensify, resulting in a decrease in the equilibrium temperature of CPH.

It is also easy to see from the results that each salt exerts a distinct effect on the phase equilibria at the same mass concentration. The mixture solution of CaCl₂-MgCl₂ shows a more significant influence compared to other solutions. By comparing the impact of molarity on the water activity (the water activity is predicted by using the geochemical model PHREEQC with the PITZER database) of salts sharing the same anion or cation group with further support from the experimental data of Ho-Van et al. [27,30], the hindering effect of cations and anions on phase equilibria is revealed (see in Appendices C and D). The impact of cations on water activity is ranked as follows: Mg²⁺ > Ca²⁺ > Na⁺ > K⁺. A comparison of the charge density of the cations Mg²⁺ (ionic radius equal 0.78 Å), Ca²⁺ (1.00 Å), Na⁺ (1.02 Å), and K⁺ (1.38 Å) reveals a direct proportionality between the charge density and the hydrate inhibition effect. It can be posited that higher charge density can lead to a stronger electrostatic interaction between the cations and the polarities of the water molecules. Therefore, the higher charge density cations (smaller, highly charged cations) have a stronger hydration shell than the lower charge density cations (larger, less charged cations). However, in the series of potassium and sodium halide experiments, the Br[−] anion shows a slightly stronger effect on the hydrate inhibition than the Cl[−] anion, while

the charge density of the Br^- anion is less than that of the Cl^- anion. Anions slow down the reorientation of the O-H groups, thereby exerting an effect on the ambient water network and resulting in the reduction in the hydrogen bonding strength of water molecules. Those trends are in good agreement with K. M. Sabil et al. ($\text{CO}_2 + \text{THF}$ hydrate in the presence of NaCl, CaCl_2 , MgCl_2 , KBr, NaF, KCl, and NaBr), M. Cha et al. (CH_4 hydrate in the presence of NaCl, KCl, and NH_4Cl), and Z. Ling et al. [39–41].

The temperature–concentration curves (Figure 7) exhibit a horizontal tendency at high concentrations for CPH in 10 wt.% K_2SO_4 and 15 wt.% $\text{CaCl}_2\text{-MgCl}_2$ solutions with the quick dissociation procedure. This is probably due to the co-precipitation of salt hydrates and hydrates [27]. When water and CP form hydrates, the residual solution will have a higher salt concentration than the prepared salt concentration value, creating favorable conditions for forming salt hydrates. As the cooling system shuts down, the CPH and the salt hydrates dissociate simultaneously. At the recorded equilibrium temperature (5.8 °C for a 10 wt.% of K_2SO_4 solution and 0.3 °C for a 15 wt.% $\text{CaCl}_2\text{-MgCl}_2$ solution), the hydrate is completely dissolved while the salt hydrate remains. Therefore, it can be deduced that this temperature is not the equilibrium temperature for the concentration of the prepared solution but for the lower one. This phenomenon should be taken into account when treating these salt systems using CPH-based technology. Other methods, such as membranes or reverse osmosis, could be combined to address this challenge and achieve the desired level of water purity [17].

To assess reproducibility, five experiments (quick dissociation, with salt mixtures: NaBr-KBr at 5 wt.%; $\text{Na}_2\text{SO}_4\text{-K}_2\text{SO}_4$ at 3.5 wt.%; $\text{CaCl}_2\text{-MgCl}_2$ at 5–10–15 wt.%) were conducted in duplicate, and the results showed an error of less than 0.1 °C.

4. Modeling CPH Thermodynamic Equilibrium

Several approaches are employed to model the phase equilibrium of CPH in the presence of salts. The first approach is based on Hildebrand and Scott's equation and is called the SFPD equation [42]. The second one, on the other hand, is based on a novel HLS correlation discovered by Hu et al. [43–46]. The third is the Kihara approach [47]. The last one is called ABOC. All these models are presented well by Ho-Van et al. in investigating CPH in saline systems [27,30].

The results comparing the methods will be reported as the AAD in temperature between the experimental data and predicted results, described as follows:

$$\text{AAD} = \frac{1}{N} \sum_{i=1}^N |T_{i,\text{pred}} - T_{i,\text{exp}}| \quad (1)$$

where N is the number of equilibrium data points, and $T_{i,\text{pred}}$ and $T_{i,\text{exp}}$ are the predicted and measured equilibrium temperature, respectively.

4.1. SFPD Approach

Ho-Van et al. [30] utilized Hildebrand and Scott's equation [42,48], which is widely employed for modeling solid–liquid equilibria of a pure solute in a solvent to express water activity in salt solution with the presence of CPH:

$$\ln a_w = \frac{\Delta H_{\text{fm}}}{R} \left(\frac{T_f - T}{T_f T} \right) + \frac{\Delta C_{\text{fm}}}{R} \left[\frac{(T_f - T)}{T} - \ln \left(\frac{T_f}{T} \right) \right] \quad (2)$$

with R as the gas constant. The water activity (a_w) can be calculated by using the geochemical model PHREEQC with the PITZER database. The fusion temperature (T_f) is 279.95 K—determined by Ho-Van et al. [30] and Nakajima et al. [49]. ΔH_{fm} is the molar enthalpy of dissociation in J/mole. The value of ΔH_{fm} is accurately determined by Naka-

jima et al. [49]. The only unknown parameter is ΔC_{fm} , the change in molar specific heat between the subcooled liquid and solid in J/mole/K.

By using the experimental equilibrium temperature of CPH in the presence of sodium chloride, Ho-Van introduced the correlation for ΔC_{fm} as follows:

$$\Delta C_{fm} = a \times \exp(b \times T) \quad (3)$$

More details on SFPD approach can be found in the references [27,30].

4.2. HLS Correlation

The HLS correlation [43–46] is based on the fundamental principle of freezing point depression, which for hydrates is equivalent to the suppression temperature from the uninhibited system. At the equilibrium hydrate dissociation, the fugacity of water in the solid (hydrate) phase and the liquid phase has to be equal.

$$f_w^s(T, P) = f_w^l(T, P) = x_w \gamma_w(T, P, x) f_w^{L_0}(T, P) \quad (4)$$

where x_w and γ_w are the mole fraction and activity coefficient of water, respectively. f represents the fugacity for solid (S), liquid (L), and pure water (L_0). The following assumptions have been considered: the system pressure and the composition of the hydrate are constant, and there are no salts present in the hydrate structure.

The ratio of the pure phase fugacity to the Gibbs energy of fusion can be expressed as follows:

$$\frac{\Delta_{fus}G(T, P)}{RT} = \ln \frac{f_w^{L_0}(T, P)}{f_w^s(T, P)} \quad (5)$$

By substituting the expression of enthalpy and entropy of fusion, we have the following:

$$\ln \frac{f_w^{L_0}(T, P)}{f_w^s(T, P)} = \frac{1}{RT} \left[\Delta_{fus}H(T_0) \left(1 - \frac{T}{T_0} \right) + \int_{T_0}^T \Delta C_p dT - T \int_{T_0}^T \frac{\Delta C_p}{T} dT \right] \quad (6)$$

with T_0 presenting the normal freezing temperature. The heat capacity difference between pure water and solid crystal is denoted by ΔC_p . The heat capacity terms are generally negligible due to their minute numerical values.

$$\ln \frac{f_w^s(T, P)}{f_w^{L_0}(T, P)} = \ln(x_w \gamma_w) = \ln(a_w) = -\frac{1}{RT} \left[\Delta_{fus}H(T_0) \left(1 - \frac{T}{T_0} \right) \right] \quad (7)$$

For gas hydrates, the enthalpy of fusion $\Delta_{fus}H$ can be replaced by hydrate dissociation enthalpy ($\Delta H_{diss} = H_{gas} + nH_{H_2O} - H_{gas \cdot nH_{H_2O}}$). Consequently, the hydrate depression temperature ($\Delta T = T_0 - T$) can be expressed by the following:

$$\frac{\Delta T}{T_0 T} = -\frac{nR}{\Delta H_{diss}} \ln a_w \quad (8)$$

where T_0 and T are the hydrate dissociation temperature with pure water and aqueous salt solution, n is the hydration number, a_w is water activity, and ΔH_{diss} is the hydrate dissociation enthalpy.

Hu et al. [43] considered the hydrate number and hydrate dissociation enthalpy to be constant. So $\beta = \frac{nR}{\Delta H_{diss}}$ is only dependent on the hydrate former and hydrate structure. Hu et al. also verified that the values of $\frac{nR}{\Delta H_{diss}}$ for sI hydrates forming from different guest molecules, such as CH_4 , ethane, and carbon dioxide, are pretty close. Therefore, $\beta_1 = \frac{nR}{\Delta H_{diss}}$ is used to present this term for hydrate sI. Finally, the value of $\frac{\Delta T}{T_0 T}$ is only a function of water

activity, which strongly depends on salt species and concentration. Effective mole fraction (X) is introduced to describe the relationship between water activity and salt concentration.

$$X = \sum_{j=\text{salts}} \sum_{i=\text{ions}} |z_{j,i}| x_{j,i} \quad (9)$$

In this equation, z indicates the ion charge number, x is the mole fraction, and i and j represent the ion and salt species, respectively.

The value of $\frac{\Delta T}{T_0 T}$ then can be expressed as a polynomial equation in X . Therefore, the HLS correlation for hydrate sI is as follows:

$$\frac{\Delta T}{T_0 T} = -\frac{nR}{\Delta H_{\text{diss}}} \ln a_w = -\beta_1 \ln a_w = C_1 X + C_2 X^2 + C_3 X^3 \quad (10)$$

with fitted coefficients $C_1 = 0.0009377$, $C_2 = -0.00267$, and $C_3 = 0.03328$ [43].

In the end, the hydrate formation temperature is as follows:

$$T = T_0 \left[1 + \left(\frac{\Delta T}{T_0 T} \right) T_0 \right]^{-1} \quad (11)$$

Furthermore, they extended the HLS correlation for sII hydrate systems. For the same salt species and concentration, the ratio of the values of $\frac{\Delta T}{T_0 T}$ for sI and sII hydrates are the following:

$$\frac{\left(\frac{\Delta T}{T_0 T} \right)_{\text{II}}}{\left(\frac{\Delta T}{T_0 T} \right)_{\text{I}}} = \frac{R \ln a_w \left(\frac{n}{\Delta H_{\text{diss}}} \right)_{\text{II}}}{R \ln a_w \left(\frac{n}{\Delta H_{\text{diss}}} \right)_{\text{I}}} = \frac{\beta_2}{\beta_1} = \alpha \quad (12)$$

Two methods were proposed to determine the value of α . The first method is based on optimizing the value of α by minimizing the difference between the predicted and experimental data of CH_4 - C_2H_6 hydrate phase equilibria; α was determined to have a value of 0.927. The second method is to evaluate the hydrate dissociation heat (measured by differential scanning calorimetry or calculated from the Clausius–Clapeyron equation) and hydration number for sII hydrate directly to calculate α from the ratio of β_1 to β_2 . This method can provide more accurate predictions if the hydrate dissociation heat and the hydration number can be precisely measured. Then, the sII hydrate dissociation temperature can be calculated from the following:

$$T = T_0 \left[1 + \alpha \left(\frac{\Delta T}{T_0 T} \right)_{\text{I}} T_0 \right]^{-1} \quad (13)$$

For CPH phase equilibria for systems containing salts, no gas molecules are considered, and the pressure dependency of CPH is negligible. Ho-Van et al. [27] checked Hu et al.'s assumption in water + CP + salt systems. They found that the parameters furnished by Hu et al. did not lead to a satisfactory simulation for CPH formation temperature. Using the experimental equilibrium temperature of CPH in the presence of NaCl, KCl, CaCl_2 , and MgCl_2 , Ho-Van found that $\frac{\Delta T}{T_0 T}$ was strongly correlated to the effective mole fraction (X) and can be expressed as follows:

$$\frac{\Delta T}{T_0 T} = 0.000956623X + 0.00059779X^2 + 0.01897593X^3 \quad (14)$$

Further details on HLS correlation can be found in the references [27,43–46].

4.3. Kihara Approach

Phase equilibria are described by the equality of chemical potentials of water in aqueous (μ_W^L) and hydrate phase (μ_W^H):

$$\mu_W^L = \mu_W^H \quad (15)$$

The thermodynamic model developed by van der Waals and Platteeuw [47] is widely used to correlate and predict clathrate hydrate equilibrium. This approach is based on the Gibbs–Duhem equation for the water liquid phase and statistical thermodynamics for the hydrate phase with the following assumptions:

- (i) Each cavity encloses only one guest molecule
- (ii) The interaction between the guest molecule and the cavity can be described by a pair of the potential functions of the pair guest molecule
- (iii) The cavities are perfectly spherical
- (iv) Guest molecules do not deform cavities
- (v) There is no interaction between the guest molecules in different cavities.

The phase equilibrium can be written by introducing a hypothetical reference state (β state), which corresponds to the hydrate phase with empty cavities:

$$\Delta\mu_W^{H-\beta} = \Delta\mu_W^{L-\beta} \quad (16)$$

with $\Delta\mu_W^{H-\beta}$ as the difference between the chemical potential of water in the hydrate phase and the potential of the hypothetical β phase. $\Delta\mu_W^{L-\beta}$ is the difference between the chemical potential of the liquid phase and the chemical potential of the hypothetical phase.

Liquid phase

As mentioned above, $\Delta\mu_W^{L-\beta}$ can then be calculated from classical thermodynamics by using the Gibbs–Duhem equation [50]:

$$\Delta\mu_W^{L-\beta} = T \frac{\Delta\mu_W^{L-\beta}|_{T^0, P^0}}{T^0} - T \int_{T^0}^T \frac{\Delta h_W^{L-\beta}|_{P^0}}{T^2} dT + \int_{P^0}^P \Delta v_W^{L-\beta}|_T dP - RT \ln a_W^L|_{T,P} \quad (17)$$

where $T_0 = 273.15$ K and $P_0 = 0$ are reference conditions. $a_W^L|_{T,P}$ is water activity in the liquid phase at the temperature T and pressure P . The water activity can be rewritten as the product of the mole fraction of water in the liquid phase (x_W^L) and the activity coefficient of water (γ_W); therefore, $a_W^L = \gamma_W x_W^L$. If the aqueous phase is considered ideal, then the activity coefficient can be set to 1, resulting in $a_W^L \cong x_W^L$. $\Delta v_W^{L-\beta}|_T$ represents the molar volume difference between the liquid and reference phase, which has been measured with high accuracy via X-ray diffraction by von Stackelberg [51]. $\Delta\mu_W^{L-\beta}|_{T^0, P^0}$ is the chemical potential difference between water in the liquid phase and water in the hydrate phase at the reference state. $\Delta h_W^{L-\beta}|_{P^0}$ is the difference between the molar enthalpy of two phases, which by Sloan [1] had been refined as follows:

$$\Delta h_{w,m}^{L-\beta}|_{P_0} = \Delta h_{w,m}^{L-\beta}|_{T_0 P_0} + \int_{T_0}^T \Delta C_{pw,m}^{L-\beta}|_{P_0} dT \quad (18)$$

By assuming linear dependence of $\Delta C_{pw,m}^{L-\beta}$ (the molar calorific capacity difference between liquid and reference phase), the following is obtained:

$$\Delta C_{pw,m}^{L-\beta}|_{P_0} = \Delta C_{pw,m}^{L-\beta}|_{T_0 P_0} + b_{p,w}^{L-\beta} (T - T_0) \quad (19)$$

Hence, the difference in the chemical potential of the liquid phase and the chemical potential of the hypothetical phase can be rewritten as follows:

$$\begin{aligned} \Delta\mu_w^{L-\beta} = & T \frac{\Delta\mu_w^{L-\beta}|_{T^0, P^0}}{T^0} + \left(b_{p,w}^{L-\beta} T_0 - \Delta C_{pw,m}^{L-\beta} \Big|_{T_0 P_0} \right) - T \ln \frac{T}{T_0} + \frac{1}{2} b_{p,w}^{L-\beta} T (T_0 - T) \\ & + \left(\Delta h_{w,m}^{L-\beta} \Big|_{T_0 P_0} + \left(b_{p,w}^{L-\beta} T_0 - \Delta C_{pw,m}^{L-\beta} \Big|_{T_0 P_0} \right) T_0 - \frac{1}{2} b_{p,w}^{L-\beta} T_0^2 \right) \left(1 - \frac{T}{T_0} \right) \\ & + \Delta v_{w,m}^{L-\beta} \Big|_{T_0} (P - P_0) - RT \ln x_w^L \end{aligned} \quad (20)$$

Sloan [1] calculated the reference properties of hydrate. Thermodynamic properties of liquid compared to the reference phase are taken from the parameter of Handa et Tse [52], which is the most suitable set for modeling pure hydrates [50]. All parameters are listed in Table 2.

Table 2. Thermodynamic and reference properties of hydrate (sII only).

Parameter	Unit	Value	Citation
$\Delta h_{w,m}^{L-\beta}$	J/mol	$\Delta h_w^{I-\beta} \Big _{T_0 P_0} - 6011$	[1]
$\Delta C_{pw,m}^{L-\beta} \Big _{T_0 P_0}$	J/mol.K	−38.12	[1]
$b_{p,w}^{L-\beta}$	J/mol.K ²	0.141	[1]
$\Delta v_{w,m}^{L-\beta} \Big _{T_0}$	10 ^{−6} m ³ /mol	4.99644	[1]
$\Delta\mu_w^{L-\beta} \Big _{T^0, P^0}$	J/mol	1068	[52]
$\Delta h_w^{I-\beta} \Big _{T_0 P_0}$	J/mol	764	[52]

Hydrate phase

In the van der Waals and Platteeuw model [47], the difference between the chemical potential of water in the hydrate phase and β phase ($\Delta\mu_w^{H-\beta}$) is expressed as follows:

$$\Delta\mu_w^{H-\beta} = RT \sum_i v_i \ln \left(1 - \sum_j \theta_j^i \right) \quad (21)$$

where R is the universal gas constant (8.314 J/mol/K). v_i is the number of cavities of type i per mole of water. In the case of CPH, $v_i = 8/136$ because CP occupies the big cavities ($5^{12}6^4$) of sII hydrates. $\theta_j^i \in [0, 1]$ is the occupancy factor of type i cavities by the CP molecule (guest molecule j). The occupancy factor is written from the Langmuir adsorption approach:

$$\theta_j^i = \frac{C_j^i f_j(T, P)}{1 + \sum_j C_j^i f_j(T, P)} \quad (22)$$

where f_j is the fugacity of the guest molecule. C_j^i is the Langmuir constant of j in cavities of type i . From the integration of the interaction potential, the Langmuir constant is expressed as follows:

$$C_j^i = \frac{4\pi}{k_B T} \int_0^{R-a} \exp \left(-\frac{w(r)}{k_B T} \right) r^2 dr \quad (23)$$

where k_B is the Boltzmann constant. r is the distance from the center of the cavity. R is the empty cavity radius, and a is the hard-core radius defined in the Kihara potential. $w(r)$ is the interaction potential between the guest molecule and the cavity based on the distance

between the guest molecule and the water molecule in the structure. The Parish and Prausnitz (or Kihara) model [53] is the most precise to determine the interaction potential.

$$w(r) = 2z\varepsilon \left[\frac{\sigma^{12}}{R^{11}r} \left(\delta^{10} + \frac{a}{R} \delta^{11} \right) - \frac{\sigma^6}{R^5r} \left(\delta^4 + \frac{a}{R} \delta^5 \right) \right] \quad (24)$$

$$\delta^N = \frac{1}{N} \left[\left(1 - \frac{r}{R} - \frac{a}{R} \right)^{-N} - \left(1 + \frac{r}{R} - \frac{a}{R} \right)^{-N} \right] \quad (25)$$

The parameters ε , σ , and a are so-called Kihara parameters. ε is the maximum attractive potential, σ is the distance from the cavity center, and a is the hard-core radius. So, the interaction potential depends on only the properties of the guest molecule (via Kihara parameters) and the geometrical properties of the cavities. Ho-Van et al. [30] sought to optimize epsilon (ε) and sigma (σ) by minimizing the AAD between the predicted and experimental dissociation temperature of CPH in the presence of NaCl (Table 3).

Table 3. Optimized Kihara parameters for CPH system [30].

Kihara Parameter	Unit	Value	Citation
a	Å	0.8968	[54]
σ	Å	2.72	[30]
ε/k_B	K	265.5	[30]

Both chemical potentials of water in the liquid and the hydrate phase (μ_W^L and μ_W^H) are the function of the temperature and the salt concentration. In the liquid phase, only the temperature and the water activity (salt concentration) are significant variables. For the hydrate part, Kihara parameters for each guest molecule are unique. Therefore, the hydrate potential is determined by the CP fugacity, which is only dependent on temperature in this case. Therefore, the temperature can be calculated from a given salt concentration through the van der Waals equation or the opposite. More details on the Kihara approach can be found in the references [27,30].

4.4. ABOC Approach

The fourth approach is analogous to the third one based on the equality of chemical potential. Instead of expressing the occupancy factor by the Langmuir adsorption approach and using the Kihara parameters (ε , σ , and a), Ho-Van et al. [30] applied a simpler approach. For the difference between the chemical potential of water in the hydrate phase and β phase ($\Delta\mu_W^{H-\beta}$), they suggested expressing the occupancy of CP by a function of the water activity. The impact of CP on hydrate chemical potential is obscured in the correlation parameters. The correlation is expressed as follows:

$$\theta(a_w) = m \times (a_w^2) + n \times (a_w) + p \quad (26)$$

Ho-Van used the experimental equilibrium temperatures of CPH in the presence of NaCl to obtain the correlation coefficients ($m = -0.0004772$, $n = 0.0004731$, and $p = 0.9998800$). Further details on the ABOC approach can be found in references [27,30].

5. Modeling Results

5.1. SFPD Approach

The equilibrium temperatures obtained from experimental data are presented alongside those predicted by the SFPD approach in Figure 9 (further details in Table 4 or Table A8, Appendix E). The AAD is 0.21 °C for the CPH in the K_2SO_4 and NaCl-NaBr solution, which

is likely similar to the case of KBr, $\text{Na}_2\text{SO}_4\text{-K}_2\text{SO}_4$, and NaBr-KBr ($0.23\text{ }^\circ\text{C}$). For the NaBr salt and the mixture of $\text{CaCl}_2\text{-MgCl}_2$, this value is $0.42\text{ }^\circ\text{C}$ and $0.27\text{ }^\circ\text{C}$, respectively. The smallest AAD is $0.20\text{ }^\circ\text{C}$ for CPH in the KCl-KBr solution. These results indicated that the phase equilibrium temperatures were adequately replicated by the SFPD approach. Nevertheless, a considerable discrepancy ($0.84\text{ }^\circ\text{C}$) was observed between the modeling and experimental data concerning 10 wt.% NaBr solution.

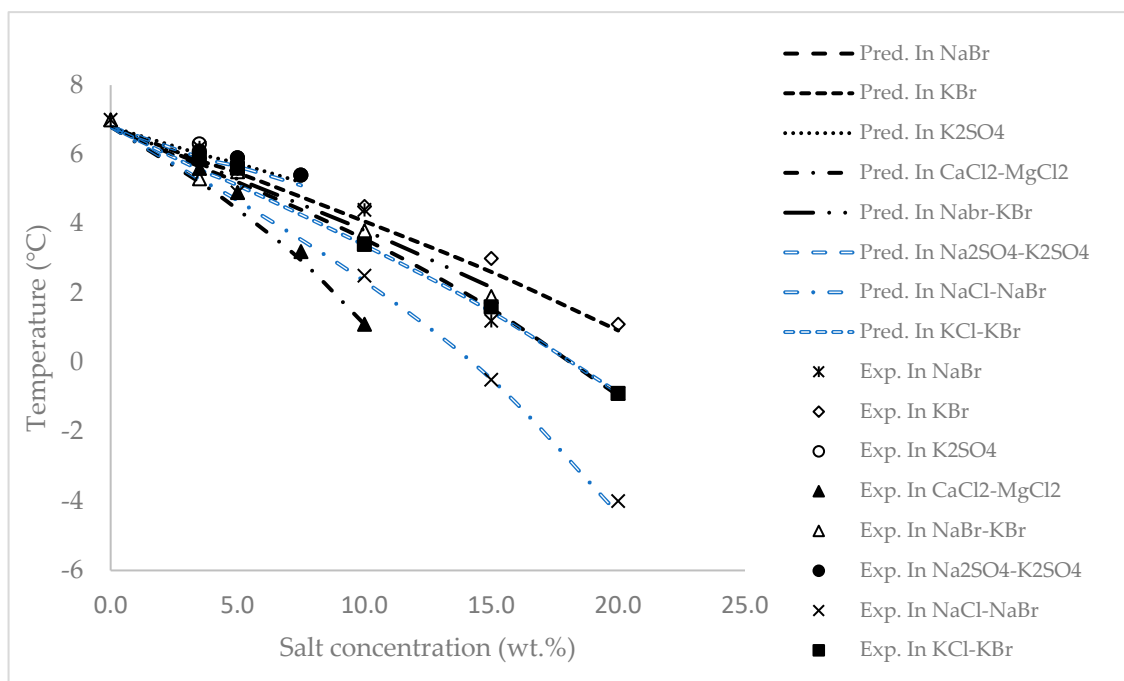


Figure 9. Experimental and predicted equilibrium temperature of CPH in the brine solution according to the SFPD approach.

Table 4. The AAD ($^\circ\text{C}$) of different approaches for predicting CPH equilibrium temperature.

	SFPD Approach	HLS Correlation	Kihara Approach	ABOC Approach
NaBr	0.42	0.42	0.24	0.38
KBr	0.23	0.23	0.25	0.25
K_2SO_4	0.21	0.69	0.31	0.10
$\text{CaCl}_2\text{-MgCl}_2$	0.27	0.76	0.11	0.27
NaBr-KBr	0.23	0.28	0.49	0.19
$\text{Na}_2\text{SO}_4\text{-K}_2\text{SO}_4$	0.23	0.79	0.28	0.12
NaCl-NaBr	0.21	0.13	0.19	0.24
KCl-KBr	0.20	0.30	0.13	0.22

5.2. HLS Correlation

Figure 10 shows the fitted polynomial line given by the equation between $\frac{\Delta T}{T_0 T}$ vs. effective mole fraction and the CPH depression temperature (experimental data) vs. the effective mole fraction of NaBr, KBr, K_2SO_4 , and mixture of $\text{CaCl}_2\text{-MgCl}_2$, NaBr-KBr, $\text{Na}_2\text{SO}_4\text{-K}_2\text{SO}_4$, NaCl-NaBr, and KCl-KBr. It is evident that the experimental data strongly converge to the fitted curve, thereby substantiating the precision of the fitted coefficients C_1 , C_2 , and C_3 .

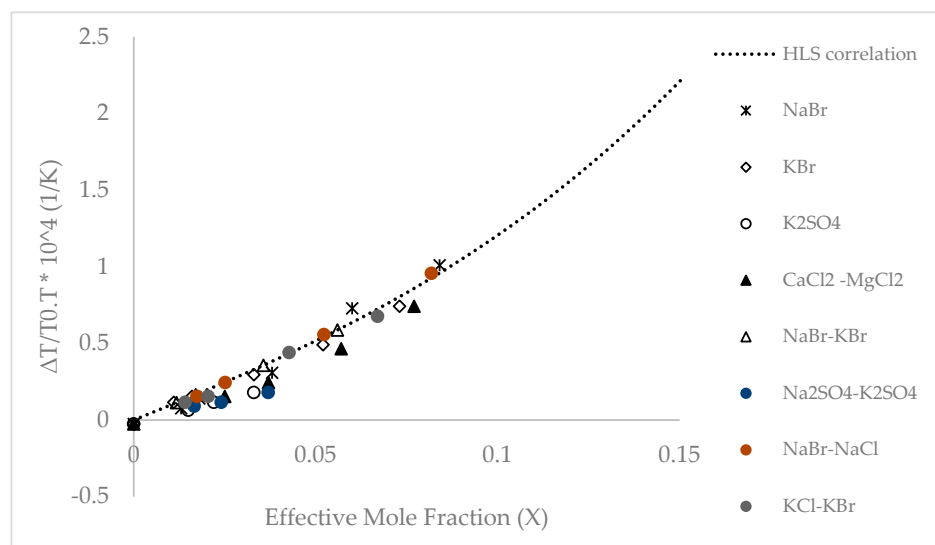


Figure 10. Experimental data of CPH in the presence of salts with the universal curve from HLS correlation of CPH hydrate.

Figure 11 presents the experimental and modeling hydrate equilibrium temperatures of the HLS correlation (more details in Table 4 or Table A8, Appendix E). Modeling results demonstrate a good agreement with the experimental equilibrium temperatures for the system containing NaBr (AAD = 0.42 °C), KBr (AAD = 0.23 °C), NaBr-KBr (AAD = 0.28 °C), NaCl-NaBr (AAD = 0.13 °C), and KCl-KBr (AAD = 0.30 °C). Unfortunately, the HLS correlation modeling method provides less reliable predictions in the case of K₂SO₄ (AAD = 0.69 °C) and the mixture of CaCl₂-MgCl₂ (AAD = 0.76 °C) and Na₂SO₄-K₂SO₄ (AAD = 0.79 °C). The inaccuracy of this method for MgCl₂ was also observed by Hu et al. [43] and Ho-Van et al. [27].

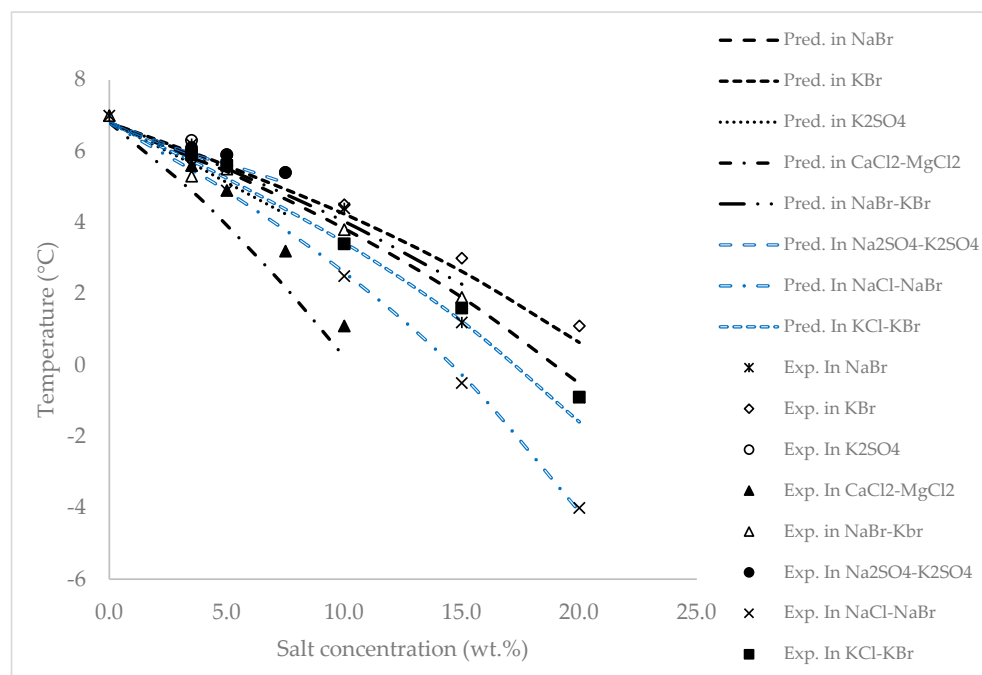


Figure 11. Experimental and predicted dissociation temperature of CPH in the brine solution according to the HLS correlation.

5.3. Kihara Approach

The Kihara modeling method shows high agreement between measured and predicted values. The maximum AAD is 0.31 °C for CPH in the presence of K_2SO_4 and 0.49 °C for CPH in the presence of NaBr-KBr. For NaBr, KBr, and Na_2SO_4 - K_2SO_4 solutions, the AADs are 0.24 °C, 0.25 °C, and 0.28 °C, respectively. Furthermore, for the mixture of $CaCl_2$ - $MgCl_2$, KCl-KBr, and NaCl-NaBr, these values are only 0.11 °C, 0.13 °C, and 0.19 °C (see Figure 12, more details in Table 4 or Table A8, Appendix E).

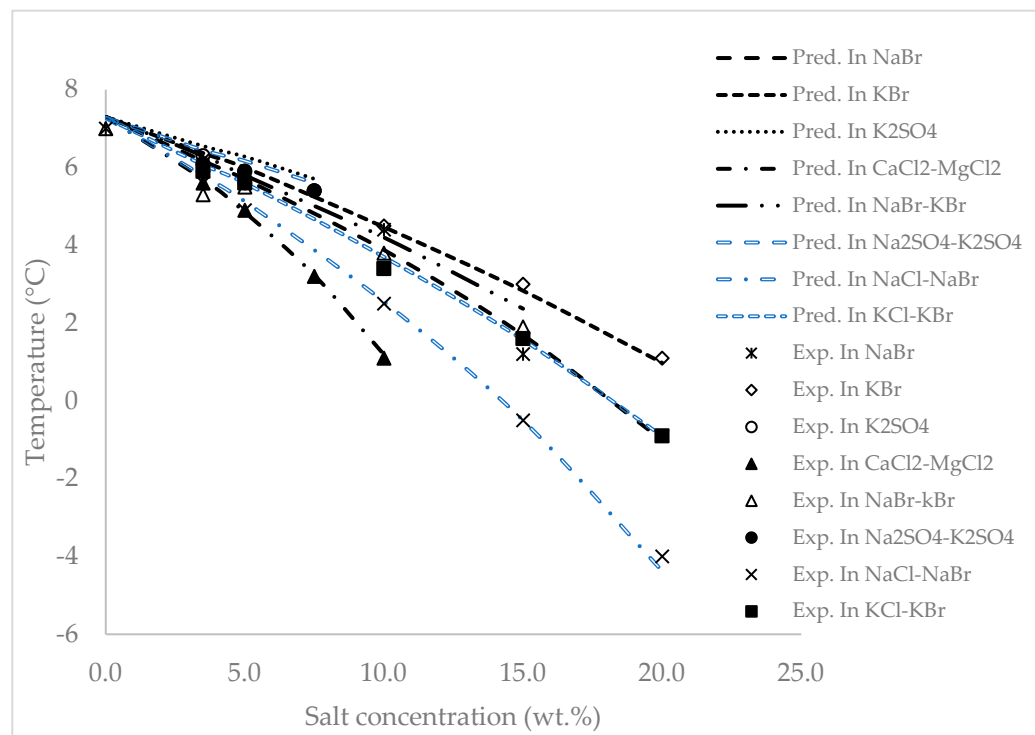


Figure 12. Experimental and predicted dissociation temperature of CPH in the brine solution according to the Kihara approach.

5.4. ABOC Approach

The results of the ABOC are shown in Figure 13 (further details in Table 4 or Table A8, Appendix E). As with the Kihara approach, the ABOC results agree well with the experimental equilibrium temperature. The AAD is about 0.10 °C for CPH in the presence of K_2SO_4 , 0.12 °C for Na_2SO_4 - K_2SO_4 , 0.19 °C for NaBr-KBr, 0.22 °C for KCl-KBr, 0.24 °C for NaCl-NaBr, 0.25 °C for KBr, 0.27 °C for $CaCl_2$ - $MgCl_2$ and about 0.38 °C for NaBr. However, the maximum AAD in this approach is 0.85 °C for 10 wt.% NaBr solution.

Table 4 lists the AAD between the results of the four simulation methods and the experimental data (additional details concerning each salt concentration are shown in Table A8, Appendix E). All four approaches demonstrate a reliable capacity to predict the hydrate formation temperature of CPH in the presence of various salts with an AAD less than or equal to 0.79 °C. The Kihara and ABOC methods yield good predictions with an AAD less than or equal to 0.49 °C and 0.38 °C, respectively. However, the ABOC method is simpler than the Kihara method. The HLS correlation is notable for its simplicity and ease of use; however, it shows relatively high AADs for certain salts, such as the Na_2SO_4 - K_2SO_4 and $CaCl_2$ - $MgCl_2$ mixture (with an AAD equal to 0.79 °C and 0.76 °C, respectively). The 10 wt.% NaBr solution exhibits significant absolute errors across all four modeling methods, likely due to experimental uncertainties (see Table A8, Appendix E). The SFPD model shows relatively good agreement with the experimental data, with an AAD of less than or

equal to 0.42 °C for all salt systems tested. Overall, the ABOC method is considered the most reliable, as it provides the most accurate data at high salt concentrations and performs reasonably well across all salt systems at lower concentrations (with an AAD less than or equal to 0.38 °C).

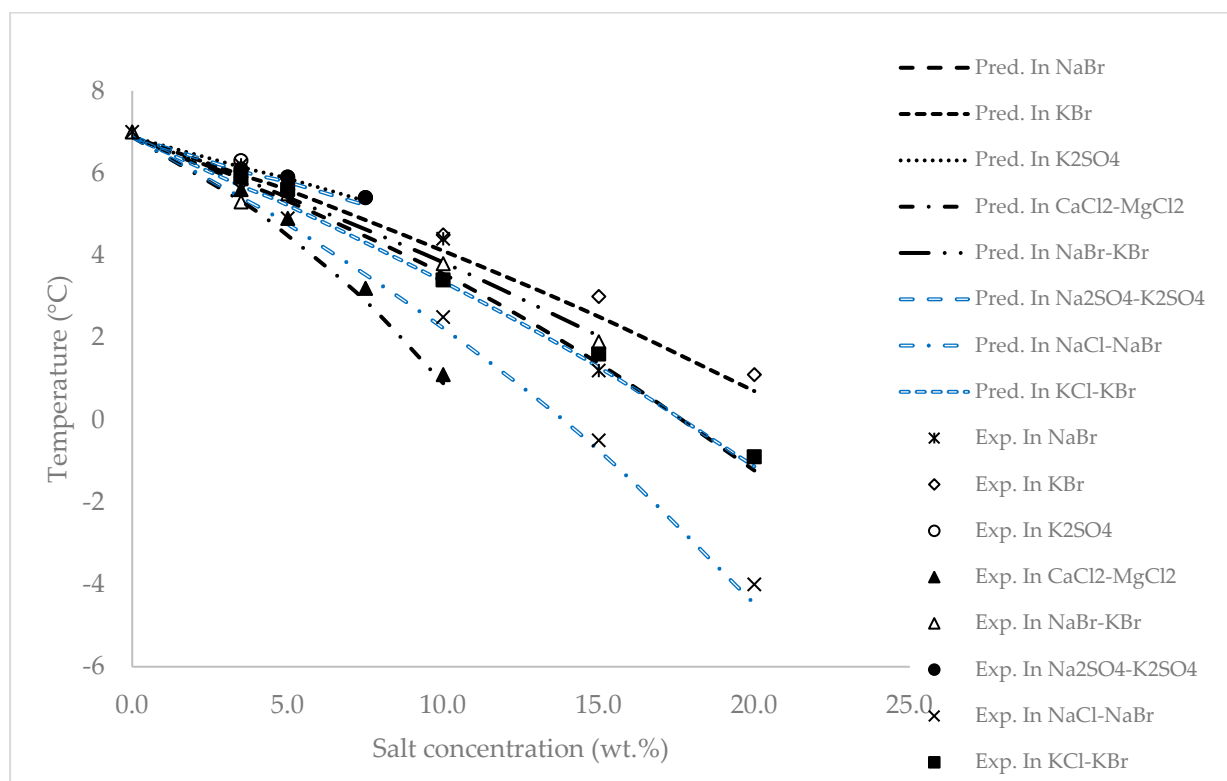


Figure 13. Experimental and predicted dissociation temperature of CPH in the brine solution according to the ABOC approach.

6. Conclusions

The thermodynamic equilibrium temperatures of CPH in saline solutions determined (by quick dissociation procedure) for NaBr (at concentrations from 3.5 wt.% to 20 wt.%), KBr (3.5 wt.% to 20 wt.%), K₂SO₄ (3.5 wt.% to 10 wt.%), CaCl₂-MgCl₂ (3.5 wt.% to 15 wt.%), NaBr-KBr (3.5 wt.% to 20 wt.%), NaCl-NaBr (3.5 wt.% to 20 wt.%), KCl-KBr (3.5 wt.% to 20 wt.%), and Na₂SO₄-K₂SO₄ (3.5 wt.% to 7.0 wt.%) ranged from 6.3 °C to 0.3 °C, 6.4 °C to 1.4 °C, 6.6 °C to 5.8 °C, 5.6 °C to 0.3 °C, 6.3 °C to 0.4 °C, 6.1 °C to −3.1 °C, 6.1 °C to −0.8 °C, and 6.4 °C to 5.5 °C, respectively. The slow procedure reported that the thermodynamic equilibrium temperatures of CPH in the presence of salts determined for NaBr (3.5 wt.% to 20 wt.%), KBr (3.5 wt.% to 20 wt.%), K₂SO₄ (3.5 wt.% to 7.5 wt.%), CaCl₂-MgCl₂ (3.5 wt.% to 10 wt.%), NaBr-KBr (3.5 wt.% to 15 wt.%), NaCl-NaBr (3.5 wt.% to 20 wt.%), KCl-KBr (3.5 wt.% to 20 wt.%), and Na₂SO₄-K₂SO₄ (3.5 wt.% to 7.0 wt.%) ranged from 6.2 °C to −0.9 °C, 5.9 °C to 1.1 °C, 6.3 °C to 5.4 °C, 5.6 °C to 1.1 °C, 5.3 °C to 1.9 °C, 5.6 °C to −4 °C, 5.9 °C to −0.9 °C, and 6.1 °C to 5.4 °C, respectively. The quick procedure data are slightly higher than the slow ones, ranging from 0 °C to 1.2 °C. This discrepancy is likely due to the inability of the quick method to reach true equilibrium, as a result of the rapid dissociation rate. Our new experimental data on CPH equilibrium in new brine solutions show excellent accuracy and reproducibility, emphasizing the reliability of our methodology and experimental systems.

The experimental results indicate that the inhibition effect of salts on hydrate's phase equilibria varies depending on salt ions and their concentration, primarily due to clustering

and salting-out phenomena. The higher initial concentration leads to a lower dissociation temperature. It is also observed that the Cl^- anion has a lesser impact on the phase equilibrium of CPH compared to the Br^- anion. Among the cations studied, Mg^{2+} cation exerts the most significant inhibitory effect on the equilibrium temperature, followed by Ca^{2+} cation, Na^+ cation, and K^+ cation, in decreasing order of influence.

The experimental results were also modeled using four different thermodynamic approaches: The SFPD approach, the HLS correlation, the Kihara approach, and the ABOC. All four modeling approaches show good agreement with the experimental data obtained from the slow dissociation procedure, with AADs less than or equal to 0.79°C . Among them, the ABOC method proves to be the most reliable for accurately predicting the equilibrium temperatures of CPH in various brine solutions (with AAD less than or equal to 0.38°C). At high salt concentrations, this model provides the most accurate data, while at low concentrations it performs reasonably well across all salt systems.

In addition, our four models have been validated and are considered reliable tools for predicting data, which is crucial for designing commercial desalination plants based on hydrates. The process operates at low temperatures and atmospheric pressure, requiring minimal energy. Moreover, it does not require specialized high-pressure equipment, allowing the use of low-cost materials and ensuring safer operation.

The future work of this study could be thermodynamic experiments, modeling on CPH in the presence of new multi-salt mixtures that are close to real seawater concentrations. The optimization of modelling is needed for CPH in the presence of all salt systems to reduce the AAD. This is important to predict the thermodynamic equilibrium points of CPH in the presence of many salt systems at a wide range of concentrations. Based on that, kinetic study can be performed and optimized at real conditions for practical HBD applications.

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Appendix A Initial Conditions for Experiments

Table A1. Initial conditions for quick dissociation procedure experiments.

No.	wt.% a,d,e	NaCl ^b (g)	NaBr ^b (g)	KBr ^b (g)	KCl ^b (g)	MgCl ₂ ^b (g)	CaCl ₂ ^b (g)	Na ₂ SO ₄ ^b (g)	K ₂ SO ₄ ^b (g)	m _{solution} ^b (g)	m _{salt add} ^b (g)	m _{ice add} ^b (g)	m _{CP} ^c (mL)
1	0.0	0	0	0	0	0	0	0	0	400	0	3	121.54
2	3.5	0	14.51	0	0	0	0	0	0	414.53	0.11	3	121.54
3	5.0	0	21.05	0	0	0	0	0	0	421.11	0.16	3	121.54
4	10.0	0	44.44	0	0	0	0	0	0	444.47	0.33	3	121.54
5	15.0	0	70.57	0	0	0	0	0	0	470.67	0.53	3	121.54
6	20.0	0	99.97	0	0	0	0	0	0	500.27	0.75	3	121.54
7	3.5	0	0	14.51	0	0	0	0	0	414.51	0.11	3	121.82
8	5.0	0	0	21.05	0	0	0	0	0	421.02	0.16	3	121.82
9	10.0	0	0	44.44	0	0	0	0	0	444.44	0.33	3	121.82
10	15.0	0	0	70.59	0	0	0	0	0	470.59	0.53	3	121.82

Table A1. Cont.

No.	wt.% a,d,e	NaCl ^b (g)	NaBr ^b (g)	KBr ^b (g)	KCl ^b (g)	MgCl ₂ ^b (g)	CaCl ₂ ^b (g)	Na ₂ SO ₄ ^b (g)	K ₂ SO ₄ ^b (g)	m _{solution} ^b (g)	m _{salt add} ^b (g)	m _{ice add} ^b (g)	m _{CP} ^c (mL)
11	20.0	0	0	100	0	0	0	0	0	500	0.75	3	121.82
12	3.5	0	0	0	0	0	0	0	14.51	414.51	0.11	3	121.82
13	5.0	0	0	0	0	0	0	0	21.05	421.05	0.16	3	121.82
14	7.5	0	0	0	0	0	0	0	32.42	432.43	0.24	3	121.82
15	10.0	0	0	0	0	0	0	0	44.44	444.44	0.33	3	121.82
16	3.5	0	0	0	0		14.51	0	0	414.51	0.11	3	121.82
17	5.0	0	0	0	0		21.05	0	0	421.05	0.16	3	121.82
18	7.5	0	0	0	0		32.43	0	0	432.43	0.33	3	121.82
19	10.0	0	0	0	0		44.44	0	0	444.44	0.53	3	121.82
20	15.0	0	0	0	0		70.59	0	0	470.59	0.75	3	121.82
21	3.5	0		14.51	0	0	0	0	0	414.51	0.11	3	121.82
22	5.0	0		21.05	0	0	0	0	0	421.05	0.16	3	121.82
23	10.0	0		44.44	0	0	0	0	0	444.44	0.33	3	121.82
24	15.0	0		70.59	0	0	0	0	0	470.59	0.53	3	121.82
25	20.0	0		100	0	0	0	0	0	500	0.75	3	121.82
26	3.5	0	0	0	0	0	0		14.51	414.51	0.11	3	121.82
27	5.0	0	0	0	0	0	0		21.05	421.05	0.16	3	121.82
28	7.5	0	0	0	0	0	0		32.43	432.43	0.24	3	121.82
29	3.5	7.25	7.25	0	0	0	0	0	0	414.5	0.11	3	121.82
30	5.0	10.53	10.53	0	0	0	0	0	0	421.06	0.16	3	121.82
31	10.0	22.22	22.22	0	0	0	0	0	0	444.44	0.33	3	121.82
32	15.0	35.29	35.29	0	0	0	0	0	0	470.58	0.53	3	121.82
33	20.0	50	50	0	0	0	0	0	0	500	0.75	3	121.82
34	3.5	0	0	7.25	7.25	0	0	0	0	414.5	0.11	3	121.82
35	5.0	0	0	10.53	10.53	0	0	0	0	421.06	0.16	3	121.82
36	10.0	0	0	22.22	22.22	0	0	0	0	444.44	0.33	3	121.82
37	15.0	0	0	35.29	35.29	0	0	0	0	470.58	0.53	3	121.82
38	20.0	0	0	50	50	0	0	0	0	500	0.75	3	121.82

Note(s): ^a Uncertainty due to weighing: $\pm 0.002\%$; ^b uncertainty due to weighing: ± 0.01 g; ^c uncertainty due to weighing: ± 0.01 mL; ^d uncertainty due to drying oven for slow dissociation procedure: $\pm 0.2\%$; ^e uncertainty due to ion chromatography: $\pm 0.015\%$.

Table A2. Initial conditions for slow dissociation procedure experiments.

No.	wt.% a,c,d,e	NaCl ^b (g)	NaBr ^b (g)	KBr ^b (g)	KCl ^b (g)	MgCl ₂ ^b (g)	CaCl ₂ ^b (g)	Na ₂ SO ₄ ^b (g)	K ₂ SO ₄ ^b (g)	m _{solution} ^b (g)	m _{salt add} ^b (g)	m _{ice add} ^b (g)	m _{CP} ^b (g)
1	0.0	0	0	0	0	0	0	0	0	600	-	5	
2	3.5	0	16.9767	0	0	0	0	0	0	485.0767	-	3.8	
3	5.0	0	30.0879	0	0	0	0	0	0	600.2	-	1.6	
4	10.0	0	60.278	0	0	0	0	0	0	602.77	-	1	
5	15.0	0	90.04	0	0	0	0	0	0	600.95	0.87	4.9	
6	20.0	0	100.367	0	0	0	0	0	0	500.17	-	1.689	
7	3.5	0	0	17.656	0	0	0	0	0	503.22	-	1.134	
8	5.0	0	0	25.104	0	0	0	0	0	500.14	-	0.976	
9	10.0	0	0	50.121	0	0	0	0	0	500.28	-	0.43	
10	15.0	0	0	75.119	0	0	0	0	0	500.11	-	0.7	
11	20.0	0	0	100.22	0	0	0	0	0	499.97	-	0.544	
12	3.5	0	0	0	0	0	0	0	21.03	600.41	-	0.5	52.67
13	5.0	0	0	0	0	0	0	0	30	600	-	1.2	52.67
14	7.5	0	0	0	0	0	0	0	45.01	600.49	-	0.2	49.45
15	3.5	0	0	0	0	10.5	10.53	0	0	601.76	-	1	48.11
16	5.0	0	0	0	0	15	15.03	0	0	603.35	-	1.16	44.28
17	7.5	0	0	0	0	22.5	22.52	0	0	600.12	-	2.4	44.15
18	10.0	0	0	0	0	30	30.01	0	0	600.52	-	1.6	48.39
19	3.5	0	17.50	17.50	0	0	0	0	0	1000.27	0	0.16	
20	5.0	0	15.00	15.02	0	0	0	0	0	600.11	0	0.26	
21	10	0	30.00	30.02	0	0	0	0	0	600.19	0	0.08	
22	15	0	45.01	44.99	0	0	0	0	0	600.04	0	0.10	
23	3.5	0	0	0	0	0	0	17.5	17.51	1000.01	-	1.18	
24	5	0	0	0	0	0	0	25.05	25	1005.82	-	1.13	
25	7.5	0	0	0	0	0	0	37.6	37.04	1000.29	-	1.06	
26	3.5	17.5	17.518	0	0	0	0	0	0	1000.05	-	0.77	
27	5	25	25	0	0	0	0	0	0	1000.08	-	0.57	
28	10	50.01	50.01	0	0	0	0	0	0	1000.53	-	0.71	
29	15	75.01	75.02	0	0	0	0	0	0	1002.73	-	1.8	
30	20	100	100.02	0	0	0	0	0	0	1000.02	-	3.32	
31	3.5	0	0	17.56	17.54	0	0	0	0	1000.05	-	1.54	
32	5	0	0	25.01	25	0	0	0	0	1000.26	-	1.06	
33	10	0	0	50	50.02	0	0	0	0	1001.37	-	1.38	
34	15	0	0	75.008	74.448	0	0	0	0	1025.25	-	1.37	
35	20	0	0	100.07	100.28	0	0	0	0	1000.35	-	1.38	

Note(s): ^a Uncertainty due to weighing: $\pm 0.002\%$; ^b uncertainty due to weighing: ± 0.01 g; ^c uncertainty due to weighing: ± 0.01 mL; ^d uncertainty due to drying oven for slow dissociation procedure: $\pm 0.2\%$; ^e uncertainty due to ion chromatography: $\pm 0.015\%$.

Appendix B Experimental Results

Table A3. Equilibrium dissociation temperature of CPH in the presence of NaBr, KBr, K₂SO₄, NaBr–KBr, NaCl–NaBr, KCl–KBr, Na₂SO₄–K₂SO₄, and CaCl₂–MgCl₂.

Solution Concentration (wt.%)								T _{e-quick} ^a (°C) (400 rpm)	T _{e-quick} ^a (°C) (500 rpm)	T _{e-slow} ^a (°C)
NaCl ^{b,c,d}	NaBr ^{b,c,d}	KBr ^{b,c,d}	KCl ^{b,c,d}	MgCl ₂ ^{b,c,d}	CaCl ₂ ^{b,c,d}	Na ₂ SO ₄ ^{b,c,d}	K ₂ SO ₄ ^{b,c,d}			
0	0	0	0	0	0	0	0	7.3	-	7
0	3.50	0	0	0	0	0	0	6.3	-	6.2
0	5.00	0	0	0	0	0	0	5.9	-	5.7
0	10.00	0	0	0	0	0	0	4.6	-	4.4
0	15.00	0	0	0	0	0	0	2.3	-	1.2
0	20.00	0	0	0	0	0	0	0.3	-	−0.9
0	0	3.50	0	0	0	0	0	6.6	6.4	5.9
0	0	5.00	0	0	0	0	0	6.2	6	5.6
0	0	10.00	0	0	0	0	0	5.2	4.7	4.5
0	0	15.00	0	0	0	0	0	3.5	3	3
0	0	20.00	0	0	0	0	0	2.3	1.4	1.1
0	0	0	0	0	0	0	3.50	6.6	6.6	6.3
0	0	0	0	0	0	0	5.00	6.4	6.2	5.9
0	0	0	0	0	0	0	7.50	-	5.9	5.4
0	0	0	0	0	0	0	10.00	-	5.8	-
0	0	0	0	1.75	1.75	0	0	-	5.6	5.6
0	0	0	0	2.50	2.50	0	0	-	4.8	4.9
0	0	0	0	3.75	3.75	0	0	-	3.3	3.2
0	0	0	0	5.00	5.00	0	0	-	1	1.1
0	0	0	0	7.50	7.50	0	0	-	0.3	-
0	1.75	1.75	0	0	0	0	0	-	6.3	5.3
0	2.50	2.50	0	0	0	0	0	-	5.8	5.5
0	5.00	5.00	0	0	0	0	0	-	4.4	3.8
0	7.50	7.50	0	0	0	0	0	-	2.4	1.9
0	10.00	10.00	0	0	0	0	0	-	0.4	-
0	0	0	0	0	0	1.75	1.75	-	6.4	6.1
0	0	0	0	0	0	2.50	2.50	-	6.1	5.9
0	0	0	0	0	0	3.75	3.75	-	5.5	5.4
1.75	1.75	0	0	0	0	0	0	-	6.1	5.6
2.50	2.50	0	0	0	0	0	0	-	5.3	4.9
5.00	5.00	0	0	0	0	0	0	-	2.7	2.5
7.50	7.50	0	0	0	0	0	0	-	−0.2	−0.5
10.00	10.00	0	0	0	0	0	0	-	−3.1	−4.0
0	0	1.75	1.75	0	0	0	0	-	6.1	5.9
0	0	2.50	2.50	0	0	0	0	-	5.5	5.6
0	0	5.00	5.00	0	0	0	0	-	3.7	3.4
0	0	7.50	7.50	0	0	0	0	-	1.2	1.6
0	0	10.00	10.00	0	0	0	0	-	−0.8	−0.9

Note(s): Where T_{e-quick} and T_{e-slow} are the equilibrium temperatures following the quick and the slow procedures;
^a uncertainty of temperature measurements: ± 0.1 °C; ^b uncertainty due to weighing: $\pm 0.002\%$; ^c uncertainty due to dry oven: $\pm 0.2\%$; ^d uncertainty due to ion chromatography: $\pm 0.015\%$.

Appendix C Equilibrium Temperature of CPH in the Presence of Na₂SO₄, CaCl₂, MgCl₂, NaCl, and KCl [27,30]

Table A4. Equilibrium temperature of CPH in the presence of Na₂SO₄, CaCl₂, MgCl₂, NaCl, and KCl.

Concentration ^{a,b,c} (wt.%)	in Na ₂ SO ₄ ^d (°C)	in CaCl ₂ ^d (°C)	in MgCl ₂ ^d (°C)	in NaCl ^d (°C)	in KCl ^d (°C)
0	7.1	7.1	7.1	7.1	7.1
1	6.7	6	6.7	6.4	6.9
2	6.4	6.3	6.2	5.9	6.1
3.5	6	5.6	5.2	5	5.5
5	5.6	4.9	4.3	4.1	4.9
6	5.3	-	-	-	-
8	-	3.3	2.1	2.4	3.6
10	-	1.8	0	0.9	2.4
12	-	0.1	−2.2	−0.4	1.4
14	-	−1.9	−5.2	−1.8	0.4
16	-	−4	−8.7	−3.8	−0.5

Table A4. Cont.

Concentration ^{a,b,c} (wt.%)	in Na ₂ SO ₄ ^d (°C)	in CaCl ₂ ^d (°C)	in MgCl ₂ ^d (°C)	in NaCl ^d (°C)	in KCl ^d (°C)
18	-	−6.7	−12.7	−5.3	−1.9
20	-	−9.6	−17.6	−7.8	−3
22	-	−13.2	-	−10.2	-
23	-	−15.1	-	−11.6	-
25	-	−19.6	-	-	-

Note(s): ^a Uncertainty due to weighing: $\pm 0.002\%$; ^b uncertainty due to dry oven: $\pm 0.2\%$; ^c uncertainty due to ion chromatography: $\pm 0.015\%$; ^d uncertainty of temperature measurements: ± 0.1 °C.

Appendix D Molarity, Water Activity, and Effective Mole Fraction

Table A5. Molarity, water activity, and effective mole fraction (X).

Concentration (wt.%)	K ₂ SO ₄			KBr			NaBr-KBr			NaBr		
	Molarity	Water Activity	X	Molarity	Water Activity	X	Molarity	Water Activity	X	Molarity	Water Activity	X
0	0	1	0	0	1	0	0	1	0	0	1	0
3.5	0.208	0.992	0.015	0.305	0.99	0.011	0.329	0.989	0.012	0.353	0.988	0.013
5	0.302	0.989	0.022	0.442	0.986	0.016	0.477	0.984	0.017	0.512	0.983	0.018
7.5	0.465	0.983	0.033	-	-	-	-	-	-	-	-	-
10	0.638	0.978	0.045	0.934	0.97	0.033	1.007	0.967	0.036	1.08	0.964	0.038
15	-	-	-	1.483	0.953	0.052	1.599	0.948	0.056	1.715	0.941	0.060
20	-	-	-	2.101	0.934	0.073	2.265	0.925	0.078	2.43	0.914	0.084

Table A6. Molarity, water activity, and effective mole fraction (X) (continued).

Concentration (wt.%)	NaCl-NaBr			KCl-KBr			CaCl ₂ -MgCl ₂			Na ₂ SO ₄ -K ₂ SO ₄		
	Molarity	Water Activity	X	Molarity	Water Activity	X	Molarity	Water Activity	X	Molarity	Water Activity	X
0	0	1	0	0	1	0	0	1	0	0	1	0
3.5	0.487	0.984	0.017	0.396	0.987	0.014	0.354	0.983	0.025	0.232	0.991	0.017
5	0.706	0.977	0.025	0.574	0.982	0.020	0.514	0.974	0.037	0.336	0.988	0.024
7.5	-	-	-	-	-	-	0.791	0.957	0.057	0.518	0.982	0.037
10	1.491	0.95	0.052	1.212	0.962	0.043	1.084	0.936	0.077	-	-	-
15	2.367	0.919	0.082	1.925	0.94	0.067	1.722	-	-	-	-	-
20	3.354	0.881	0.114	2.727	0.915	0.094	-	-	-	-	-	-

Table A7. Molarity, water activity, and effective mole fraction (X) (continued).

wt.%	Na ₂ SO ₄			CaCl ₂			MgCl ₂			NaCl			KCl		
	Molarity	Water Activity	X	Molarity	Water Activity	X	Molarity	Water Activity	X	Molarity	Water Activity	X	Molarity	Water Activity	X
0	0	1	0	0	1	0	0	1	0	0	1	0	0	1	0
1	0.071	0.997	0.005	0.091	0.996	0.007	0.106	0.995	0.008	0.173	0.994	0.0062	0.135	0.996	0.0049
2	0.144	0.994	0.01	0.184	0.991	0.013	0.214	0.99	0.015	0.349	0.989	0.0125	0.274	0.991	0.0098
3.5	0.255	0.99	0.018	0.327	0.984	0.023	0.381	0.981	0.027	0.621	0.98	0.0221	0.487	0.984	0.0174
5	0.371	0.986	0.027	0.474	0.977	0.034	0.553	0.971	0.039	0.901	0.971	0.0319	0.706	0.978	0.0251
6	0.449	0.984	0.032	-	-	-	0.67	-	0.048	-	-	-	-	-	-
8	-	-	-	0.784	0.959	0.056	0.913	0.947	0.065	1.489	0.951	0.0522	1.166	0.963	0.0411
10	-	-	-	1.001	0.944	0.071	1.167	0.926	0.082	1.903	0.937	0.0662	1.49	0.954	0.0523
12	-	-	-	1.229	0.927	0.087	1.432	0.902	0.101	2.335	0.922	0.0807	1.829	0.943	0.0638
14	-	-	-	1.467	0.907	0.103	1.71	0.872	0.119	2.788	0.906	0.0956	2.184	0.932	0.0756
16	-	-	-	1.716	0.885	0.12	2.001	0.838	0.139	3.262	0.888	0.1109	2.555	0.921	0.0879
18	-	-	-	1.978	0.859	0.138	2.306	0.798	0.159	3.759	0.869	0.1267	2.944	0.909	0.1007
20	-	-	-	2.253	0.83	0.156	2.626	0.751	0.181	4.281	0.848	0.1431	3.353	0.896	0.1139
22	-	-	-	-	-	-	-	-	-	4.83	0.824	0.16	-	-	-
23	-	-	-	-	-	-	-	-	-	5.115	0.812	0.1686	-	-	-

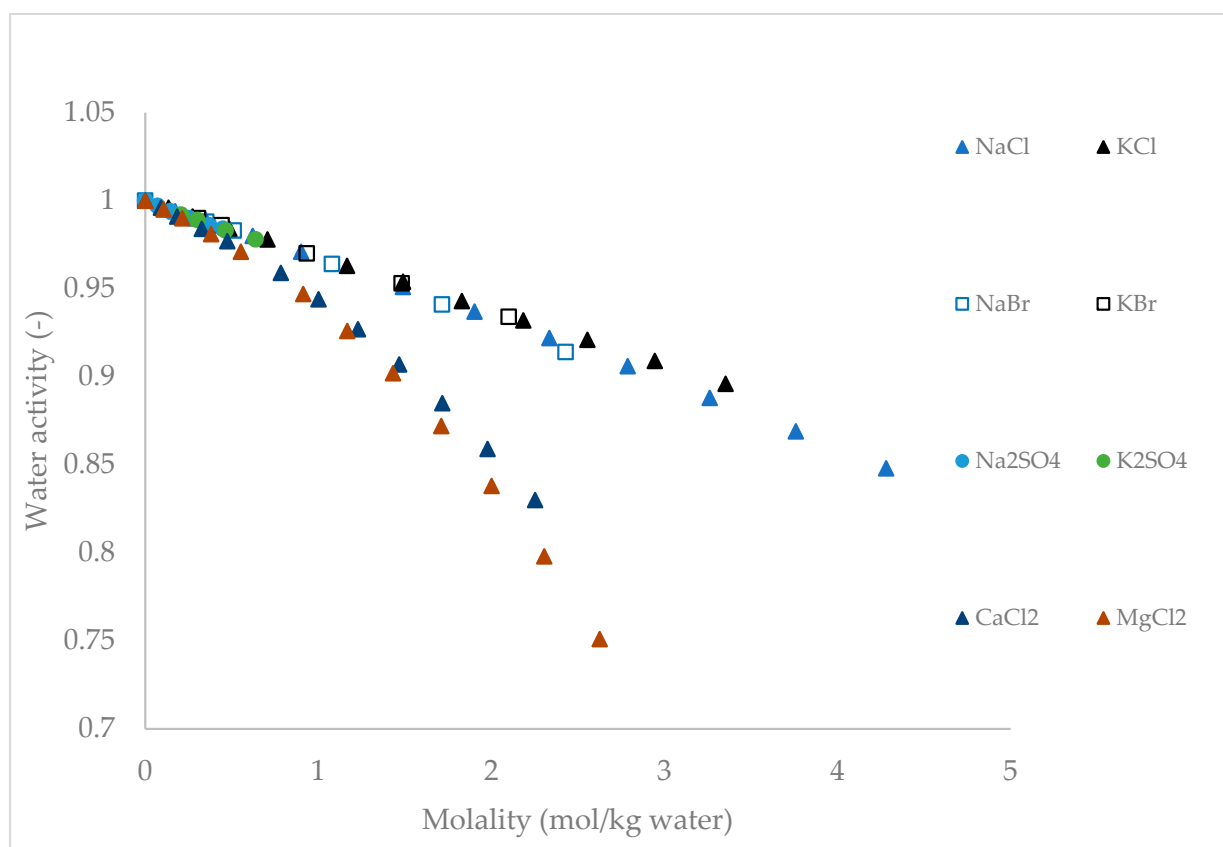


Figure A1. Water activity vs. molality of CPH in the presence of salts.

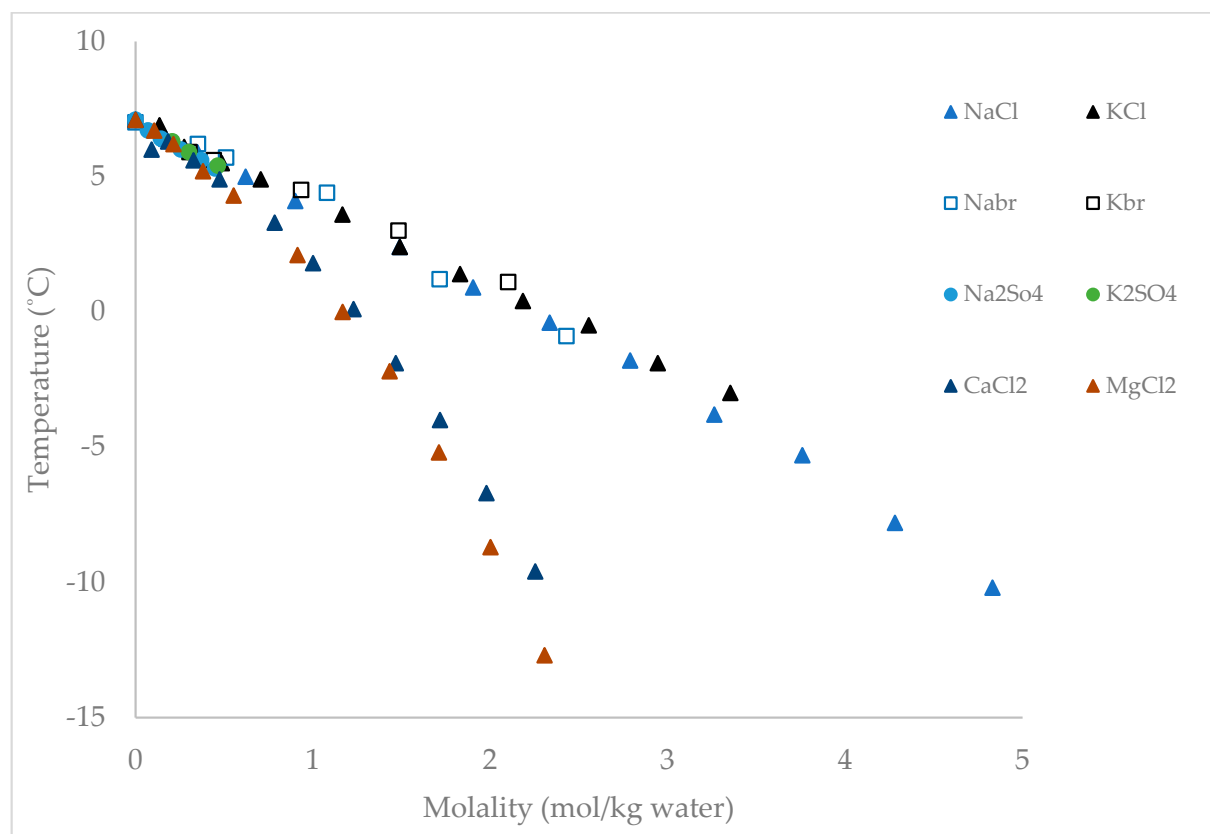


Figure A2. Temperature vs. molality of CPH in the presence of salts.

Appendix E Modeling Results of CPH in the Presence of Salts

Table A8. Modeling results of CPH in the presence of salts.

Solution Concentration (wt.%)									SFPD		HLS		Kihara		ABOC	
NaCl (wt.%)	NaBr (wt.%)	KBr (wt.%)	KCl (wt.%)	MgCl ₂ (wt.%)	CaCl ₂ (wt.%)	Na ₂ SO ₄ (wt.%)	K ₂ SO ₄ (wt.%)	Texp (°C)	Tpred (°C)	ΔT (°C)	Tpred (°C)	ΔT (°C)	Tpred (°C)	ΔT (°C)	Tpred (°C)	ΔT (°C)
0	0	0	0	0	0	0	0	7	6.8	0.2	6.8	0.2	7.3	0.3	6.88	0.12
0	3.50	0	0	0	0	0	0	6.2	5.65	0.55	5.82	0.38	6.17	0.03	5.78	0.42
0	5.00	0	0	0	0	0	0	5.7	5.2	0.5	5.43	0.27	5.7	0.00	5.32	0.38
0	10.00	0	0	0	0	0	0	4.4	3.56	0.84	3.83	0.57	3.88	0.52	3.55	0.85
0	15.00	0	0	0	0	0	0	1.2	1.55	0.35	1.9	0.7	1.69	0.49	1.37	0.17
0	20.00	0	0	0	0	0	0	−0.9	−0.96	0.06	−0.51	0.39	−1.01	0.11	−1.23	0.33
								AAD	0.42		AAD	0.42	AAD	0.24	AAD	0.38
0	0	3.50	0	0	0	0	0	5.9	5.83	0.07	5.97	0.07	6.37	0.47	5.96	0.06
0	0	5.00	0	0	0	0	0	5.6	5.47	0.13	5.59	0.01	6	0.4	5.59	0.01
0	0	10.00	0	0	0	0	0	4.5	4.07	0.43	4.24	0.26	4.47	0.03	4.11	0.39
0	0	15.00	0	0	0	0	0	3	2.61	0.39	2.63	0.37	2.83	0.17	2.51	0.49
0	0	20.00	0	0	0	0	0	1.1	0.92	0.18	0.64	0.46	0.98	0.12	0.70	0.40
								AAD	0.23		AAD	0.23	AAD	0.25	AAD	0.25
0	0	0	0	0	0	0	3.50	6.3	6.02	0.28	5.66	0.64	6.55	0.25	6.15	0.15
0	0	0	0	0	0	0	5.00	5.9	5.74	0.16	5.12	0.78	6.28	0.38	5.87	0.03
0	0	0	0	0	0	0	7.50	5.4	5.2	0.2	4.24	1.16	5.71	0.31	5.32	0.08
								AAD	0.21		AAD	0.69	AAD	0.31	AAD	0.10
0	0	0	0	1.75	1.75	0	0	5.6	5.2	0.4	4.89	0.71	5.7	0.1	5.32	0.28
0	0	0	0	2.50	2.50	0	0	4.9	4.41	0.49	3.92	0.98	4.85	0.05	4.48	0.42
0	0	0	0	3.75	3.75	0	0	3.2	2.95	0.25	2.18	1.02	3.23	0.03	2.89	0.31
0	0	0	0	5.00	5.00	0	0	1.1	1.1	0.00	0.23	0.87	1.19	0.09	0.89	0.21
								AAD	0.27		AAD	0.76	AAD	0.11	AAD	0.27
0	1.75	1.75	0	0	0	0	0	5.3	5.74	0.44	5.91	0.61	6.30	1.00	5.87	0.57
0	2.50	2.50	0	0	0	0	0	5.5	5.29	0.21	5.51	0.01	5.80	0.30	5.41	0.09
0	5.00	5.00	0	0	0	0	0	3.8	3.81	0.01	4.03	0.23	4.20	0.40	3.83	0.03
0	7.50	7.50	0	0	0	0	0	1.9	2.17	0.27	2.27	0.37	2.37	0.47	2.04	0.14
								AAD	0.23		AAD	0.28	AAD	0.49	AAD	0.19
0	0	0	0	0	0	1.75	1.75	6.1	5.92	0.18	5.54	0.56	6.45	0.35	6.05	0.05
0	0	0	0	0	0	2.50	2.50	5.9	5.65	0.25	4.96	0.94	6.17	0.27	5.78	0.12
0	0	0	0	0	0	3.75	3.75	5.4	5.11	0.29	3.92	1.48	5.60	0.20	5.22	0.18
								AAD	0.23		AAD	0.79	AAD	0.28	AAD	0.12
1.75	1.75	0	0	0	0	0	0	5.6	5.29	0.31	5.48	0.12	5.79	0.19	5.41	0.19
2.50	2.50	0	0	0	0	0	0	4.9	4.67	0.23	4.88	0.02	5.13	0.23	4.76	0.14
5.00	5.00	0	0	0	0	0	0	2.5	2.34	0.16	2.6	0.10	2.55	0.05	2.23	0.27
7.50	7.50	0	0	0	0	0	0	−0.5	−0.48	0.02	−0.27	0.23	−0.50	0.00	−0.74	0.24
10.00	10.00	0	0	0	0	0	0	−4.0	−4.36	0.36	−4.1	0.10	−4.37	0.37	−4.47	0.47
								AAD	0.21		AAD	0.13	AAD	0.19	AAD	0.24
0	0	1.75	1.75	0	0	0	0	5.9	5.56	0.34	5.73	0.17	6.07	0.17	5.69	0.21
0	0	2.50	2.50	0	0	0	0	5.6	5.11	0.49	5.24	0.36	5.60	0.00	5.22	0.38
0	0	5.00	5.00	0	0	0	0	3.4	3.38	0.02	3.44	0.04	3.70	0.30	3.36	0.04
0	0	7.50	7.50	0	0	0	0	1.6	1.46	0.14	1.23	0.37	1.57	0.03	1.28	0.32
0	0	10.00	10.00	0	0	0	0	−0.9	−0.87	0.03	−1.59	0.69	−0.90	0.00	−1.13	0.23
								AAD	0.20		AAD	0.30	AAD	0.13	AAD	0.22

References

- Sloan, E.D.; Koh, C.A. *Clathrate Hydrates of Natural Gases*, 3rd ed.; CRC Press: Boca Raton, FL, USA, 2007.
- Sloan, E.D. Fundamental principles and applications of natural gas hydrates. *Nature* **2003**, *426*, 353–359. [\[CrossRef\]](#)
- Koh, C.A.; Sloan, E.D.; Sum, A.K.; Wu, D.T. Fundamentals and applications of gas hydrates. *Annu. Rev. Chem. Biomol. Eng.* **2011**, *2*, 237–257. [\[CrossRef\]](#)
- Sloan, E.D.; Koh, C.A.; Sum, A.; Ballard, A.L.; Creek, J.L.; Eaton, M.; Lachance, J.; McMullen, N.; Palermo, T.; Shoup, G.; et al. *Natural Gas Hydrates in Flow Assurance*; Gulf Professional Publishing (Elsevier): Oxford, UK, 2011.
- Mimachi, H.; Takeya, S.; Yoneyama, A.; Hyodo, K.; Takeda, T.; Gotoh, Y.; Murayama, T. Natural gas storage and transportation within gas hydrate of smaller particle: Size dependence of self-preservation phenomenon of natural gas hydrate. *Chem. Eng. Sci.* **2014**, *118*, 208–213. [\[CrossRef\]](#)
- Sun, Z.G.; Wang, R.; Ma, R.; Guo, K.; Fan, S. Natural gas storage in hydrates with the presence of promoters. *Energy Convers. Manag.* **2003**, *44*, 2733–2742. [\[CrossRef\]](#)
- Burnol, A.; Thion, I.; Ruffine, L.; Herri, J.M. Influence of impurities (nitrogen and methane) on the CO₂ storage capacity as sediment-hosted gas hydrates—Application in the area of the Celtic Sea and the Bay of Biscay. *Int. J. Greenh. Gas Control* **2015**, *35*, 96–109. [\[CrossRef\]](#)
- Babu, P.; Linga, P.; Kumar, R.; Englezos, P. A review of the hydrate based gas separation (HBGS) process for carbon dioxide pre-combustion capture. *Energy* **2015**, *85*, 261–279. [\[CrossRef\]](#)
- Herslund, P.J.; Thomsen, K.; Abildskov, J.; von Solms, N.; Galfré, A.; Brântuas, P.; Kwaterski, M.; Herri, J.-M. Thermodynamic promotion of carbon dioxide-clathrate hydrate formation by tetrahydrofuran, cyclopentane and their mixtures. *Int. J. Greenh. Gas Control* **2013**, *17*, 397–410. [\[CrossRef\]](#)

10. Herri, J.-M.; Bouchemoua, A.; Kwaterski, M.; Brântuas, P.; Galfré, A.; Bouillot, B.; Douzet, J.; Ouabbas, Y.; Cameirao, A. Enhanced selectivity of the separation of CO₂ from N₂ during crystallization of semi-clathrates from quaternary ammonium solutions. *Oil Gas Sci. Technol.* **2014**, *69*, 947–968. [\[CrossRef\]](#)
11. Poothia, T.; Mehra, D.; Singh, J.; Rawat, P.B.S.; Pandey, G. Role of CO₂ Capture and Sequestration (CCS) Using Gas Hydrate Based Technology for Sustainable Energy. *Energy Proc.* **2021**, *20*, 548. [\[CrossRef\]](#)
12. Duc, N.H.; Chauvy, F.; Herri, J.M. CO₂ capture by hydrate crystallization—A potential solution for gas emission of steelmaking industry. *Energy Convers. Manag.* **2007**, *48*, 1313–1322. [\[CrossRef\]](#)
13. Yin, Z.; Zheng, J.; Kim, H.; Seo, Y.; Linga, P. Hydrates for cold energy storage and transport: A review. *Adv. Appl. Energy* **2021**, *2*, 100022. [\[CrossRef\]](#)
14. Hashemi, H.; Babaee, S.; Mohammadi, A.H.; Naidoo, P.; Ramjugernath, D. Experimental study and modeling of the kinetics of refrigerant hydrate formation. *J. Chem. Thermodyn.* **2015**, *82*, 47–52. [\[CrossRef\]](#)
15. Wang, X.; Dennis, M.; Hou, L. Clathrate hydrate technology for cold storage in air conditioning systems. *Renew. Sustain. Energy Rev.* **2014**, *36*, 34–51. [\[CrossRef\]](#)
16. Hong, S.; Moon, S.; Lee, Y.; Lee, S.; Park, Y. Investigation of thermodynamic and kinetic effects of cyclopentane derivatives on CO₂ hydrates for potential application to seawater desalination. *Chem. Eng. J.* **2019**, *363*, 99–106. [\[CrossRef\]](#)
17. Ho-Van, S.; Bouillot, B.; Douzet, J.; Babakhani, S.M.; Herri, J.M. Cyclopentane hydrates—A candidate for desalination? *J. Environ. Chem. Eng.* **2019**, *7*, 103359. [\[CrossRef\]](#)
18. Zhang, J.; Chen, S.; Mao, N.; He, T. Progress and prospect of hydrate-based desalination technology. *Front. Energy* **2022**, *16*, 445–459. [\[CrossRef\]](#)
19. Sahu, P.; Krishnaswamy, S.; Ponnani, K.; Pande, N.K. A thermodynamic approach to selection of suitable hydrate formers for seawater desalination. *Desalination* **2018**, *436*, 144–151. [\[CrossRef\]](#)
20. Lv, Y.N.; Wang, S.S.; Sun, C.Y.; Gong, J.; Chen, G.J. Desalination by forming hydrate from brine in cyclopentane dispersion system. *Desalination* **2017**, *413*, 217–222. [\[CrossRef\]](#)
21. Serikkali, A.; Van, H.N.; Pham, T.-K.; Le, Q.D.; Douzet, J.; Herri, J.-M.; Bouillot, B. Phase equilibrium and dissociation enthalpies of CO₂/cyclopentane hydrates in presence of salts for water treatment and CO₂ capture: New experimental data and modeling. *Fluid Phase Equilib.* **2022**, *556*, 113410. [\[CrossRef\]](#)
22. Xu, H.; Khan, M.N.; Peters, C.J.; Sloan, E.D.; Koh, C.A. Hydrate-Based Desalination Using Cyclopentane Hydrates at Atmospheric Pressure. *J. Chem. Eng. Data* **2018**, *63*, 1081–1087. [\[CrossRef\]](#)
23. Lee, J.; Kim, K.S.; Seo, Y. Thermodynamic, structural, and kinetic studies of cyclopentane + CO₂ hydrates: Applications for desalination and CO₂ capture. *Chem. Eng. J.* **2019**, *375*, 121974. [\[CrossRef\]](#)
24. Han, S.; Rhee, Y.W.; Kang, S.P. Investigation of salt removal using cyclopentane hydrate formation and washing treatment for seawater desalination. *Desalination* **2017**, *404*, 132–137. [\[CrossRef\]](#)
25. Ahmadpanah, S.J.; Manteghian, M.; Ganji, H. Effect of cyclopentane on hydrate-based desalination efficiency at different operating condition. *J. Taiwan Inst. Chem. Eng.* **2023**, *143*, 104653. [\[CrossRef\]](#)
26. Parker, A. Potable water from sea-water. *Nature* **1942**, *149*, 184–186. [\[CrossRef\]](#)
27. Ho-Van, S.; Bouillot, B.; Douzet, J.; Babakhani, S.M.; Herri, J.M. Implementing Cyclopentane Hydrates Phase Equilibrium Data and Simulations in Brine Solutions. *Ind. Eng. Chem. Res.* **2018**, *57*, 14774–14783. [\[CrossRef\]](#)
28. Hassanpouryouzband, A.; Joonaki, E.; Farahani, M.V.; Takeya, S.; Ruppel, C.; Yang, J.; English, N.J.; Schicks, J.M.; Edlmann, K.; Mehrabian, H.; et al. Gas hydrates in sustainable chemistry. *Chem. Soc. Rev.* **2020**, *49*, 5225–5309. [\[CrossRef\]](#)
29. Mezher, T.; Fath, H.; Abbas, Z.; Khaled, A. Techno-economic assessment and environmental impacts of desalination technologies. *Desalination* **2011**, *266*, 263–273. [\[CrossRef\]](#)
30. Ho-Van, S.; Bouillot, B.; Douzet, J.; Babakhani, S.M.; Herri, J.M. Experimental measurement and thermodynamic modeling of cyclopentane hydrates with NaCl, KCl, CaCl₂, or NaCl-KCl present. *AIChE J.* **2018**, *64*, 2207–2218. [\[CrossRef\]](#)
31. Kamochi, K.; Tripathi, A.; Taoka, M.; Ohmura, R.; Yasuda, K. Phase equilibrium conditions in cyclopentane hydrate forming systems coexisting with sodium chloride aqueous solution under atmospheric pressure and vacuum condition. *J. Chem. Thermodyn.* **2022**, *175*, 106886. [\[CrossRef\]](#)
32. Zylyftari, G.; Lee, J.W.; Morris, J.F. Salt effects on thermodynamic and rheological properties of hydrate forming emulsions. *Chem. Eng. Sci.* **2013**, *95*, 148–160. [\[CrossRef\]](#)
33. Baek, S.; Min, J.; Lee, J.W. Equilibria of cyclopentane hydrates with varying HLB numbers of sorbitan monoesters in water-in-oil emulsions. *Fluid Phase Equilib.* **2016**, *413*, 41–47. [\[CrossRef\]](#)
34. Kishimoto, M.; Iijima, S.; Ohmura, R. Crystal growth of clathrate hydrate at the interface between seawater and hydrophobic-guest liquid: Effect of elevated salt concentration. *Ind. Eng. Chem. Res.* **2012**, *51*, 5224–5229. [\[CrossRef\]](#)
35. Sakemoto, R.; Sakamoto, H.; Shiraiwa, K.; Ohmura, R.; Uchida, T. Clathrate Hydrate Crystal Growth at the Seawater/Hydrophobic–Guest–Liquid Interface. *Cryst. Growth Des.* **2010**, *10*, 1296–1300. [\[CrossRef\]](#)

36. Delroisse, H.; Torr , J.P.; Dicharry, C. Effect of a hydrophilic cationic surfactant on cyclopentane hydrate crystal growth at the water/cyclopentane interface. *Cryst. Growth Des.* **2017**, *17*, 5098–5107. [[CrossRef](#)]
37. McAuliffe, C. Solubility in water of paraffin, cycloparaffin, olefin, acetylene, cycloolefin, and aromatic hydrocarbons. *J. Phys. Chem.* **1966**, *70*, 1267–1275. [[CrossRef](#)]
38. Dean, J.A. LANGE’S HANDBOOK OF CHEMISTRY. *Mater. Manuf. Process.* **1990**, *5*, 687–688. [[CrossRef](#)]
39. Sabil, K.M.; Rom n, V.R.; Witkamp, G.J.; Peters, C.J. Experimental observations on the competing effect of tetrahydrofuran and an electrolyte and the strength of hydrate inhibition among metal halides in mixed CO₂ hydrate equilibria. *J. Chem. Thermodyn.* **2010**, *42*, 400–408. [[CrossRef](#)]
40. Cha, M.; Hu, Y.; Sum, A.K. Methane hydrate phase equilibria for systems containing NaCl, KCl, and NH₄Cl. *Fluid Phase Equilib.* **2016**, *413*, 2–9. [[CrossRef](#)]
41. Ling, Z.; Shi, C.; Li, F.; Fu, Y.; Zhao, J.; Dong, H.; Yang, Y.; Zhou, H.; Wang, S.; Song, Y. Desalination and Li⁺ enrichment via formation of cyclopentane hydrate. *SePurif. Technol.* **2020**, *231*, 115921. [[CrossRef](#)]
42. Hildebrand, J.H.; Scott, R.L. *Regular Solutions*; Prentice-Hall International Series in Chemistry; Prentice-Hall, Inc.: Englewood Cliffs, NJ, USA, 1962.
43. Hu, Y.; Lee, B.R.; Sum, A.K. Universal correlation for gas hydrates suppression temperature of inhibited systems: I. Single salts. *AIChE J.* **2017**, *63*, 5111–5124. [[CrossRef](#)]
44. Hu, Y.; Lee, B.R.; Sum, A.K. Universal correlation for gas hydrates suppression temperature of inhibited systems: II. Mixed salts and structure type. *AIChE J.* **2018**, *64*, 2240–2250. [[CrossRef](#)]
45. Hu, Y.; Sa, J.; Lee, B.R.; Sum, A.K. Universal correlation for gas hydrates suppression temperature of inhibited systems: III. salts and organic inhibitors. *AIChE J.* **2018**, *64*, 4097–4109. [[CrossRef](#)]
46. Sa, J.H.; Sum, A.K. Universal correlation for gas hydrates suppression temperature of inhibited systems: IV. Water activity. *AIChE J.* **2021**, *67*, e17293. [[CrossRef](#)]
47. van der Waals, J.H.; Platteeuw, J.C. Clathrate Solutions. *Adv. Chem. Phys.* **1958**, *2*, 1–57. [[CrossRef](#)]
48. Miyawaki, O.; Saito, A.; Matsuo, T.; Nakamura, K. Activity and Activity Coefficient of Water in Aqueous Solutions and Their Relationships with Solution Structure Parameters. *Biosci. Biotechnol. Biochem.* **1997**, *61*, 466–469. [[CrossRef](#)]
49. Nakajima, M.; Ohinura, R.; Mori, Y.H. Clathrate hydrate formation from cyclopentane-in-water emulsions. *Ind. Eng. Chem. Res.* **2008**, *47*, 8933–8939. [[CrossRef](#)]
50. Herri, J.M.; Bouchemoua, A.; Kwaterski, M.; Fezoua, A.; Ouabbas, Y.; Cameirao, A. Gas hydrate equilibria for CO₂-N₂ and CO₂-CH₄ gas mixtures-Experimental studies and thermodynamic modelling. *Fluid Phase Equilib.* **2011**, *301*, 171–190. [[CrossRef](#)]
51. Stackelberg, M.V.; M ller, H.R. On the Structure of Gas Hydrates. *J. Chem. Phys.* **1951**, *19*, 1319–1320. [[CrossRef](#)]
52. Handa, Y.P.; Tse, J.S. Thermodynamic properties of empty lattices of structure I and structure II clathrate hydrates. *J. Phys. Chem.* **1986**, *90*, 5917–5921. [[CrossRef](#)]
53. Parrish, W.R.; Prausnitz, J.M. Dissociation Pressures of Gas Hydrates Formed by Gas Mixtures. *Ind. Eng. Chem. Process Des. Dev.* **1972**, *11*, 26–35. [[CrossRef](#)]
54. Takeuchi, F.; Ohmura, R.; Yasuoka, K. Statistical-thermodynamics modeling of clathrate-hydrate-forming systems suitable as working media of a hydrate-based refrigeration system. *Int. J. Thermophys.* **2009**, *30*, 1838–1852. [[CrossRef](#)]

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